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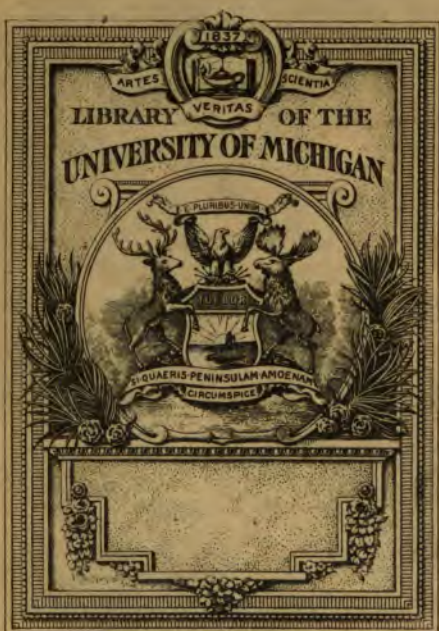
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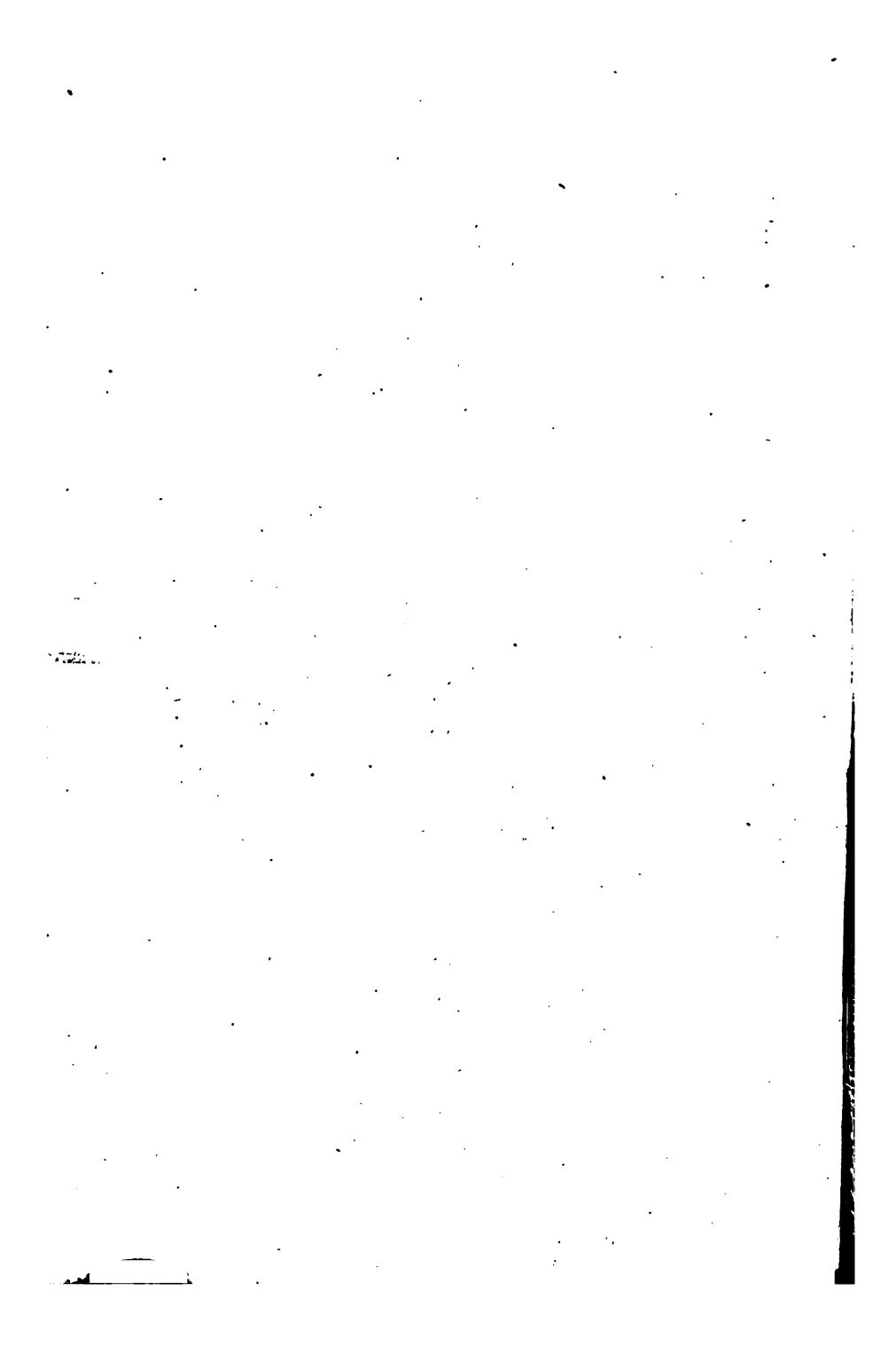
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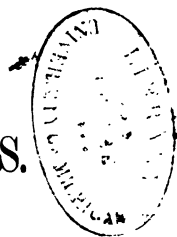
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LECTURE NOTES
FOR
CHEMICAL STUDENTS.



BY
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ERRATUM.

Page 169, line 5 from bottom, for "eleven" read "fourteen."

LECTURE NOTES

FOR

CHEMICAL STUDENTS.

ORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

THE name *organic* is commonly restricted, by chemists, to compounds the molecules of which consist of one or more atoms of carbon *directly* combined either with carbon, nitrogen, or hydrogen. Thus, according to this definition, carbonic anhydride ($O=C=O$) and hydric potassic carbonate ($H-O-C-O-K$) are mineral or inorganic compounds,



because the carbon which they contain is directly combined with oxygen only; but oxalic acid ($\begin{array}{c} O=C-O-H \\ | \\ O=C-O-H \end{array}$), cyanic acid ($N\equiv C-O-H$), and formic acid ($O=C-O-H$) are



organic compounds, because their molecules contain carbon directly combined, in the first case with carbon, in the second with nitrogen, and in the third with hydrogen.

The number of elements usually entering into the composition of organic compounds is very small.

A large number of these compounds consist of carbon united with only *one* other element, either hydrogen or, rarely, nitrogen.

The members of another very large class contain only *three* elements:—carbon, hydrogen, and oxygen; carbon, hydrogen, and nitrogen; or carbon, nitrogen, and oxygen.

Others contain *four* elements—carbon, hydrogen, oxygen, and nitrogen.

Some contain sulphur, chlorine, bromine, iodine, silicon, phosphorus, boron, or metals ; but these are comparatively rare.

Although the number of the elements entering into the composition of organic compounds is much smaller than that usually taking part in the formation of minerals, yet the complexity of the former class of compounds is frequently much greater.

There is no instance of an organic molecule containing but two single atoms, and only one containing three (hydrocyanic acid, HCN).

On the other hand, the number of atoms in a single organic molecule is sometimes very great. Thus :—

The molecule of Spermaceti contains 98 atoms.

| | | | | | |
|---|---|----------|---|-----|---|
| " | " | Stearin | " | 178 | " |
| " | " | Margarin | " | 217 | " |
| " | " | Albumen | " | 226 | " |
| " | " | Protagon | " | 384 | " |

In nearly all organic compounds *carbon is a tetrad*. It forms, therefore, with 1 atom of hydrogen a triad compound radical, which exists in chloroform ($\text{C}^{\text{iv}}\text{H}$) $^{\text{iii}}$ Cl_3 ; a dyad compound radical with 2 atoms of hydrogen, as in methylenic dichloride ($\text{C}^{\text{iv}}\text{H}_2$) $^{\text{ii}}$ Cl_2 ; and a monad compound radical with 3 atoms of hydrogen, as in methylic iodide ($\text{C}^{\text{iv}}\text{H}_3$) $^{\text{i}}$ I . But in these compounds it will be seen that the carbon is always saturated and always a tetrad.

This is in conformity with the following general law :—"In every molecule of a chemical compound the sum of the bonds is always an even number," because every number, whether odd or even, when multiplied by 2 gives an even number. To this may be added the following law, to which no exception is known :—"The sum of the bonds in any molecule is at least twice as great as the active atomicity of the most polyad element in the compound."

A compound organic radical is a group of atoms containing one

or more atoms of carbon of which one or more bonds are unsatisfied; and it is either a monad, dyad, &c. radical, according to the number of monad atoms required to complete its active atomicity.

Such a radical, when a monad, triad, or pentad, cannot exist as a separate group; like hydrogen or nitrogen, when isolated, it combines with another group of atoms like itself, forming a duplex molecule. It is only by this union of two semi-molecules that the vacated bonds can be satisfied.

The following are two of the principal series of compound organic radicals:—

| Monads. | | Dyads. | |
|------------|--|---------------|--|
| Methyl... | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{Me} \\ \text{Me} \end{array} \right\}$ | Methylene... | CH_2 or Me''^* . |
| Ethyl ... | $\left\{ \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{Et} \\ \text{Et} \end{array} \right\}$ | Ethylene ... | C_2H_4 or Et'' . |
| Propyl ... | $\left\{ \begin{array}{l} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{Pr} \\ \text{Pr} \end{array} \right\}$ | Propylene ... | C_3H_6 or Pr'' . |
| Butyl ... | $\left\{ \begin{array}{l} \text{C}_4\text{H}_9 \\ \text{C}_4\text{H}_9 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{Bu} \\ \text{Bu} \end{array} \right\}$ | Butylene ... | C_4H_8 or Bu'' . |
| Amyl ... | $\left\{ \begin{array}{l} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{Ay} \\ \text{Ay} \end{array} \right\}$ | Amylene ... | C_5H_{10} or Ay'' . |

Organic radicals are the analogues of the monad, dyad, and triad elements of mineral chemistry.

Such being the constitution of the organic radicals, we will now proceed to investigate their functions in organic compounds, and to examine the general plan upon which these compounds are, on the atomic hypothesis, built up.

We shall be assisted in our investigation if we reduce the formulæ of these compounds to a few types or fundamental forms. In doing this it is necessary to avoid, as far as possible, all empirical grouping of atoms. Our formulæ ought to express, as exactly as possible, how the elements are combined with each other. Thus in a compound containing $\text{C}_x\text{H}_y\text{O}_z$, the formula ought to show, first, whether the hydrogen is combined with carbon or with oxygen; or if combined with both, it should indicate how many atoms are united with carbon, and how

* Only known in combination.

many with oxygen. Secondly, the formula ought to show whether the oxygen is united with carbon or with hydrogen, or partly with the one and partly with the other, or, lastly, whether it is performing the function of linking hydrogen to carbon.

This information is most completely given, in notation, by making carbon the dominant or grouping element in non-nitrogenous compounds, and nitrogen in the remaining organic compounds.

Non-nitrogenous organic compounds, exclusive of organo-metallic bodies and organo-boron and silicon compounds, can be conveniently considered under the two following types, viz. :—

- | | |
|--|--|
| 1. The monadelphic, or marsh-gas } type | $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ |
| 2. The diadelphic, or methyl type ... | $\begin{array}{cc} \text{H} & \text{H} \\ & \\ \text{H}-\text{C} & -\text{C}-\text{H} \\ & \\ \text{H} & \text{H} \end{array}$ |

Nitrogenous organic compounds arrange themselves in the most convenient manner under the two following types:—

- | | |
|-------------------------------------|---|
| 3. The ammonia type | $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ |
| 4. The ammoniac-chloride type | $\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{N}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ |

In addition to these types a few others will be occasionally necessary, such as :—

- | | |
|-------------------------------|---|
| 5. The triadelphic type | $\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\ & & \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\ & & \\ \text{H} & \text{H} & \text{H} \end{array}$ |
|-------------------------------|---|

6. The double monadelphic type ... $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$
7. The condensed diadelphic or }
olefine type..... } $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$

Double, and sometimes even treble ammonia and ammonio-chloride types are required for certain compounds, but they do not need special description here.

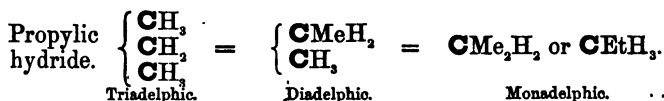
The above types are written symbolically as follows:—

1. Monadelphic type..... CH_3 .
2. Diadelphic type $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right.$.
3. Ammonia type..... $\text{N}^{\text{'''}}\text{H}_3$.
4. Ammonio-chloride type $\text{N}^{\text{H}}\text{H}_3\text{Cl}$.
5. Triadelphic type $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_3 \end{array} \right.$.
6. Double monadelphic type $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{CH}_3 \end{array} \right.$.
7. Condensed diadelphic type " $\left\{ \begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array} \right.$.

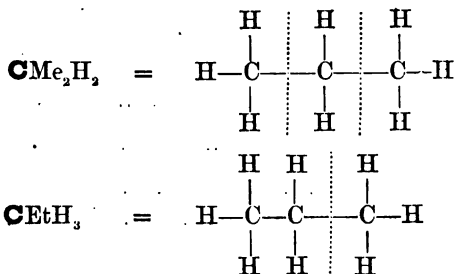
In order to facilitate the use of these symbolic types, it is advisable to become familiarized with the symbols of the following analogues of hydroxyl, in addition to those already given for inorganic compound radicals at p. 28 of vol. i., and for the monad and dyad radicals at p. 3 of the present volume:—

- | | |
|----------------|---|
| Methoxyl | CH_3O or Meo. |
| Ethoxyl | $\text{C}_2\text{H}_5\text{O}$ or Eto. |
| Propoxyl..... | $\text{C}_3\text{H}_7\text{O}$ or Pro. |
| Butoxyl | $\text{C}_4\text{H}_9\text{O}$ or Buo. |
| Amoxyl | $\text{C}_5\text{H}_{11}\text{O}$ or Ayo. |

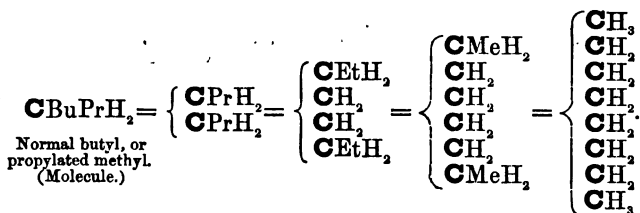
Formulae written on the triadelphic type can be reduced to the diadelphic type, and those on the latter to the monadelphic type, as follows :—



The above alternative monadelphic formulae, although apparently different, are in reality identical, as can be easily proved by expressing both graphically, thus :—

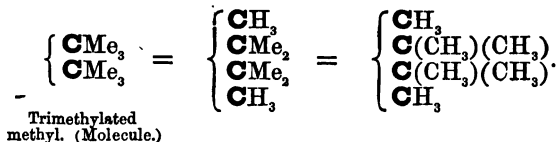
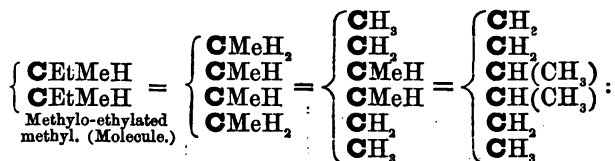


On the other hand, monadelphic formulae, if they contain a sufficient number of carbon atoms, can be expanded into diadelphic, triadelphic, &c. formulae in the following manner :—

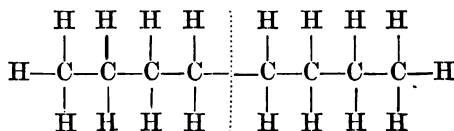


This development of normal butyl depends on the following facts :—1st, that normal butyl is propylated methyl ; 2nd, that normal propyl is ethylated methyl ; and 3rd, that ethyl is methylated methyl.

Secondary and tertiary organic radicals (see p. 10) cannot be completely developed vertically :—

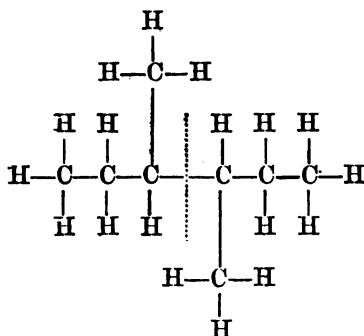


It will be seen, on comparing the above formulæ with the graphic representation of the respective compounds, that both express the same ideas of constitution. Thus in the developed symbolic formula of normal butyl it is evident that the two extreme carbon atoms are each united with three atoms of hydrogen and one of carbon, and all the intermediate carbon atoms with two of hydrogen and two of carbon, exactly as shown in the following graphic representation :—



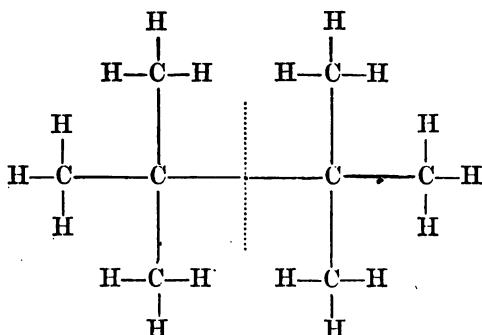
Normal butyl or propylated methyl. (Molecule.)

From the developed symbolic formula of methylo-ethylated methyl, it is evident that the two central carbon atoms are united with three atoms of carbon and one of hydrogen, that the two extreme carbon atoms are united with one atom of carbon and three of hydrogen, that the intermediate carbon atoms are joined to two hydrogen and two carbon atoms, and that the remaining carbon atoms are each combined with one atom of carbon, and three of hydrogen, thus :—



Methylo-ethylated methyl. (Molecule.)

Lastly, in the developed symbolic formula for trimethylated methyl, the two central atoms of carbon are each united with four carbon atoms, and all the remaining atoms of carbon are united with three of hydrogen and one of carbon, thus:—



Trimethylated methyl. (Molecule.)

CLASSIFICATION OF ORGANIC COMPOUNDS.

The most important organic compounds can be conveniently divided into the following thirteen families:—

1. Organic radicals.
2. Hydrides of organic radicals.

3. Alcohols.
 4. Ethers.
 5. Haloid ethers.
 6. Aldehydes,
 7. Acids.
 8. Anhydrides,
 9. Ketones,
 10. Ethereal salts.
 11. Organic compounds containing triad or pentad nitrogen,
 12. Organo-boron and silicon compounds,
 13. Organo-metallic bodies.
-

CHAPTER II.

ORGANIC RADICALS.

This family of organic compounds is divided into two classes:—

Class I. Positive radicals.

Class II. Negative radicals,

CLASS I.

POSITIVE RADICALS.

Monads.

Methyl or $(C_nH_{2n+1})_2$ Series.

Vinyl or $(C_nH_{2n-1})_2$ Series.

Phenyl or $(C_nH_{2n-7})_2$ Series,

Dyads.

Ethylene or C_nH_{2n} Series.

Acetylene or C_nH_{2n-2} Series.

Phenylene or C_nH_{2n-8} Series.

Triads.

Glyceryl or $(C_nH_{2n-1})'''_2$ Series,

CLASS I.

POSITIVE RADICALS.

MONADS.

METHYL or $(C_nH_{2n+1})_2$ SERIES.

These radicals are divided into three sections, viz. Normal, Secondary, and Tertiary :—

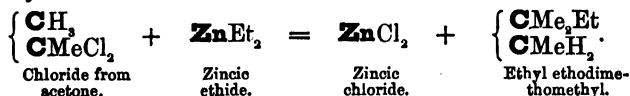
| | General formulæ. |
|----------------------------|--|
| 1. Normal Radicals | $\begin{cases} C(C_nH_{2n+1})H_2 \\ C(C_nH_{2n+1})H_2 \end{cases}$ |
| 2. Secondary Radicals ... | $\begin{cases} C(C_nH_{2n+1})_2H \\ C(C_nH_{2n+1})_2H \end{cases}$ |
| 3. Tertiary Radicals | $\begin{cases} C(C_nH_{2n+1})_3 \\ C(C_nH_{2n+1})_3 \end{cases}$ |

In the first of the above formulæ n may = 0, but in the others it must be a positive integer.

Examples of the tertiary series of radicals may be seen in the tertiary fatty acids. They have not yet been isolated.

It is evident that, besides the three series of radicals shown above, three other series, containing, in the same molecule, normal and secondary, normal and tertiary, and secondary and tertiary radicals, may exist; but up to the present time only one or two examples of such radicals are known.

By the action of zinc ethide on the chloride obtained from acetone by means of phosphoric chloride, a hydrocarbon is obtained, which may be regarded as a mixed normal and tertiary monad positive radical: ethyl etho-dimethomethyl or ethyl isoamyl :—



1. Normal Radicals.

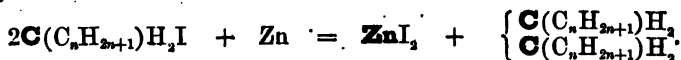
This series contains the radicals of the methylic series of alcohols.

These radicals also enter into the composition of the normal series of fatty acids.

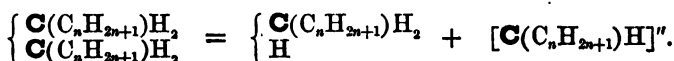
The following list contains all the radicals of this section that have been hitherto obtained :—

| | | | Boiling- points. |
|---------|-------|---|--------------------------|
| Methyl | | $\left\{ \begin{array}{l} \text{Me} \\ \text{Me} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array} \right\}$ | not known. |
| Ethyl | | $\left\{ \begin{array}{l} \text{Et} \\ \text{Et} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{CMeH}_2 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \right\}$ |about -23° . |
| Propyl | | $\left\{ \begin{array}{l} \text{Pr} \\ \text{Pr} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CEtH}_2 \\ \text{CEtH}_2 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{CH}_3 \end{array} \right\}$ | $+68^\circ$. |
| Butyl | | $\left\{ \begin{array}{l} \text{Bu} \\ \text{Bu} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CPrH}_2 \\ \text{CPrH}_2 \end{array} \right\}$ | 119° . |
| Amyl | | $\left\{ \begin{array}{l} \text{Ay} \\ \text{Ay} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CBuH}_2 \\ \text{CBuH}_2 \end{array} \right\}$ | 159° . |
| Caproyl | | $\left\{ \begin{array}{l} \text{Cp} \\ \text{Cp} \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CAyH}_2 \\ \text{CAyH}_2 \end{array} \right\}$ | 202° . |

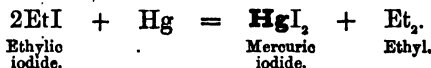
Preparation.—1. By the action of zinc on the iodides of the normal radicals :—



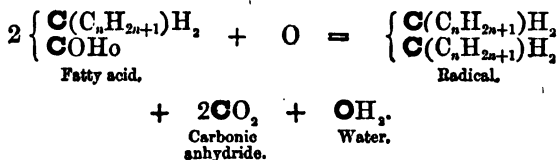
Part of the liberated radical is at the same time decomposed into the hydride of the radical and the corresponding dyad radical :—



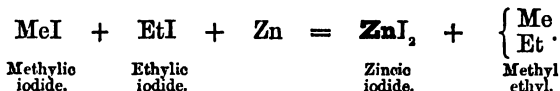
A remarkable special method for preparing ethyl consists in exposing mercury and ethylic iodide to the influence of sunlight :—



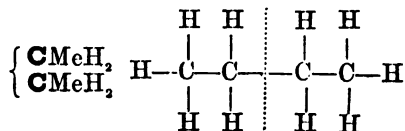
2. By the electrolysis of the salts of the normal fatty acids. In this process, nascent oxygen acts upon the fatty acid, converting its oxatyl into carbonic anhydride, the positive radical being set free:—



3. By acting with zinc upon the iodides of two radicals simultaneously, the so-called double or mixed radicals are produced:—

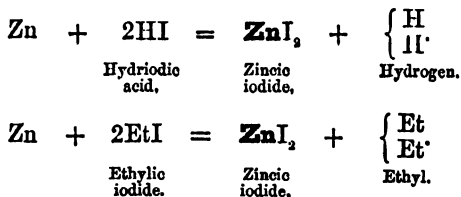


ETHYL,



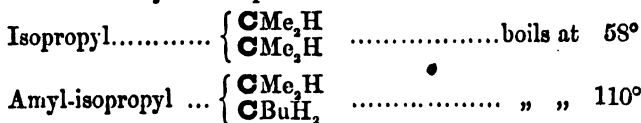
Molecular weight = 58. *Molecular volume* $\square\square$. 1 litre of ethyl gas weighs 29 criths. *Boils at about* -23°C .

Preparation.—By digesting together in a close vessel at 120° ethyl iodide and zinc, the reaction being similar to that between hydriodic acid and zinc:—

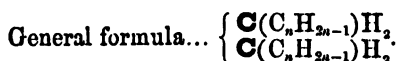


2. Secondary Radicals.

Two secondary monad positive radicals are known :—

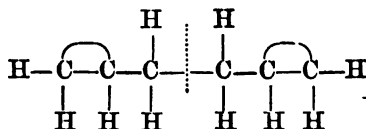
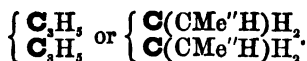


VINYL SERIES.



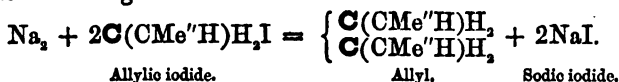
The first member of this series, vinyl, has not yet been isolated.

ALLYL.



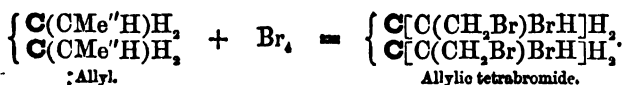
Molecular weight = 82. *Molecular volume* $\square\square$. 1 litre of allyl vapour weighs 41 criths. *Sp.gr.* 0.684. *Boils at* 59°.

Preparation.—By digesting allylic iodide with sodium, and then distilling :—



Character.—Bromine and iodine unite directly with allyl, producing allylic tetrabromide and tetriodide. In these compounds the molecule of allyl plays the part of a tetrad radical.

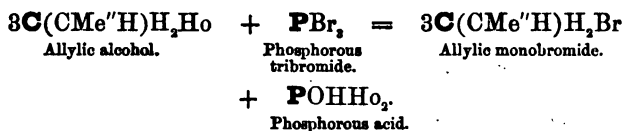
In allylic tetrabromide, four latent carbon bonds in the molecule of allyl have become active, and have united with four atoms of bromine :—



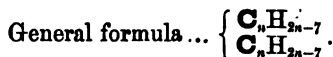
An analogous case is met with in ferric chloride, where two tetrad atoms, united by one bond of each, become together hexadic:—



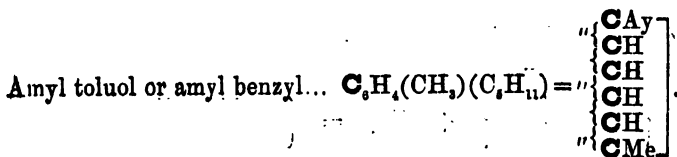
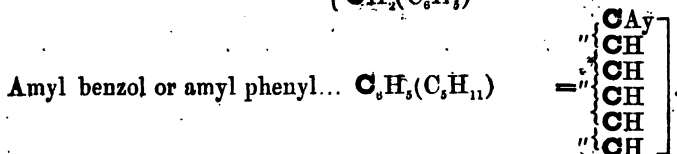
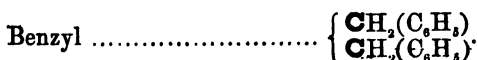
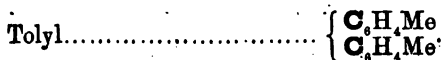
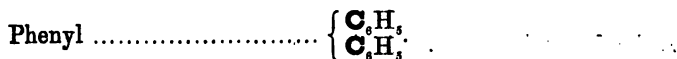
Allylic monobromide can only be obtained by the action of phosphorous tribromide on allylic alcohol:—

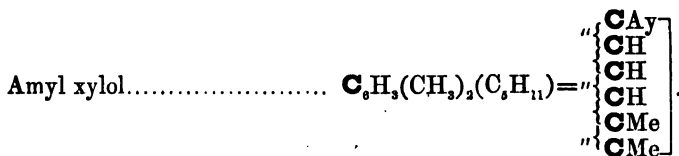


PHENYL SERIES.

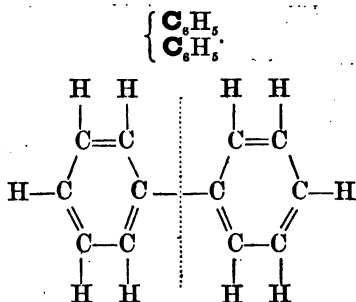


These radicals are but imperfectly known. The following have been isolated:—



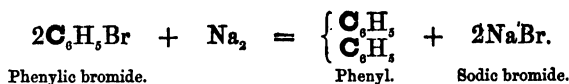


PHENYL.

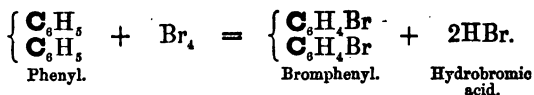


Molecular weight = 154. *Molecular volume* $\square\square$. 1 litre of phenyl vapour weighs 77 criths. *Fuses at* 70° . *Boils at* 240° .

Preparation.—By the action of sodium on phenylic bromide :—



Reaction.—By treatment with bromine, phenyl produces bromphenyl and hydrobromic acid :—



CHAPTER III.

POSITIVE RADICALS.

DYADS.

ETHYLENE or $C_n H_{2n}$ SERIES.

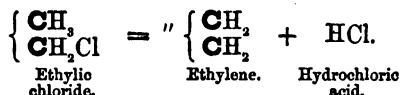
Preparation.—These compounds are produced as follows:—

1. In many cases of destructive distillation, where, however, the reaction cannot be traced.

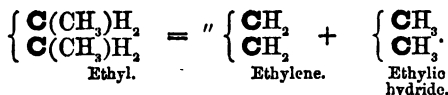
2. By the abstraction of the elements of water from the normal monohydric alcohols of the methylic series, as for instance:—



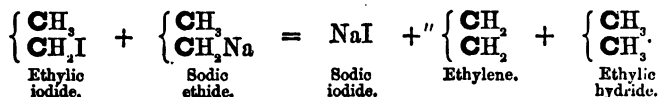
3. By passing the vapours of the haloid compounds of the normal monad radicals of the $C_n H_{2n+1}$ series over heated limo, thus:—



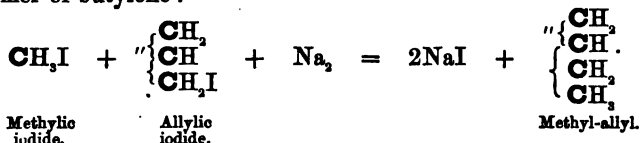
4. By the transformation of the monad radicals at the moment of liberation from their compounds, when they split into dyad radicals and the hydrides of monad radicals:—



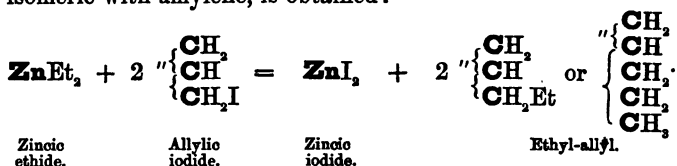
5. By the action of the iodide of a monad radical on the sodium compound of a monad radical:—



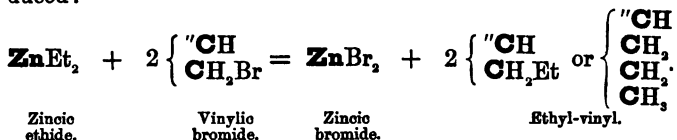
6. Methylic iodide and allylic iodide dissolved in ether and digested with sodium in sealed vessels produce methyl-allyl, an isomer of butylene :—



7. By the action of zinc ethide on allylic iodide, ethyl-allyl, isomeric with amylene, is obtained :—



8. By treatment of vinylic bromide (brominated ethylene) with zinc ethide, ethyl-vinyl, isomeric with butylene, is produced :—



Methyl-allyl differs from ethyl-vinyl.

Character.—The lower members of this series of dyad radicals are gaseous, the higher solid, and the intermediate ones liquid.

The following list includes the known dyad radicals of this series, together with their fusing- and boiling-points :—

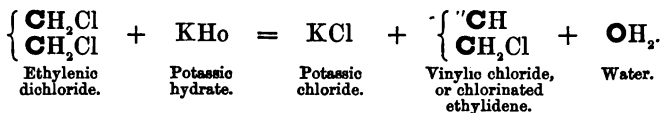
| | | Fusing-point. | Boiling-point. |
|----------------------|---------------------------------|---------------|----------------|
| Ethylene | C_2H_4 | — | — |
| Propylene | C_3H_6 | — | -17.8 |
| Pseudobutylene | C_4H_8 | — | -7.0 |
| Isobutylene | C_4H_8 | — | -5.0 |
| Butylene | C_4H_8 | — | $+3.0$ |
| Amylene | C_5H_{10} | — | 35.0 |
| Hexylene | C_6H_{12} | — | 39.0 |

| | | Fusing-point. | Boiling-point. |
|-----------------------------|------------------------------------|---------------|----------------|
| Heptylene or Enanthylene... | C_7H_{14} | — | 55.0° |
| Octylene or Caprylene..... | C_8H_{16} | — | 95.0 |
| Nonylene | C_9H_{18} | — | 125 |
| Paramylene | $\text{C}_{10}\text{H}_{20}$ | — | — |
| Cetene | $\text{C}_{18}\text{H}_{32}$ | — | — |
| Cerotene | $\text{C}_{27}\text{H}_{54}$ | 57° | 275 |
| Melene | $\text{C}_{30}\text{H}_{60}$ | 62 | 375. |

Reactions.—1. The dyad radicals of this series all unite directly with chlorine, bromine, and iodine, producing compounds which, in the case of ethylene, are represented by



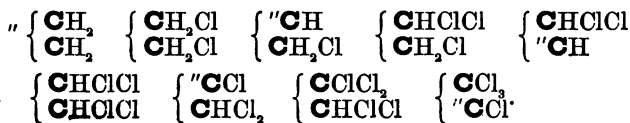
These compounds, when treated with alcoholic solution of potassic hydrate, lose one molecule of a hydracid, thus :—



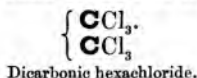
The monochlorinated radical thus obtained again unites with two atoms of chlorine, producing chlorinated ethylenic dichloride,



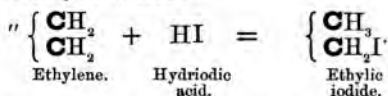
which, by further treatment with alcoholic potash, yields dichlorinated ethyldene; and so, by alternate treatments with chlorine and potassic hydrate, ethylene becomes transformed into tetrachlorinated ethyldene. The following formulæ show the first, intermediate, and final compounds :—



Tetrachlorinated ethylidene absorbs two additional atoms of chlorine, producing the solid dicarbonic hexachloride:—



2. The dyad radicals of the ethylene series can be transformed into the monad radicals from which they are derived. If ethylene be digested with hydriodic acid for 50 hours at 100° C., it is transformed into ethylic iodide:—

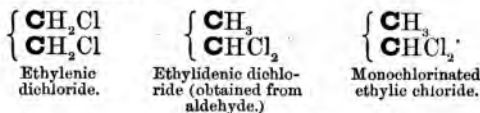


From this, ethyl may be prepared, as shown at p. 12.

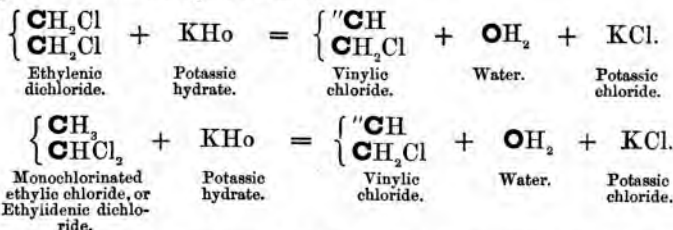
Isomerism of ethylene and ethylidene compounds.—The chlorides of the dyad radicals are isomeric:—

1. With the chlorides of the monochlorinated normal monad radicals.

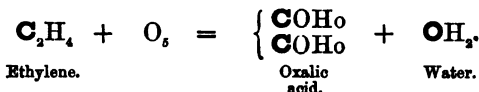
2. With the chlorides derived from the aldehydes, which, however, are identical with the chlorides of the monochlorinated normal monad radicals:—



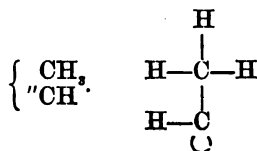
These substances, when treated with alcoholic potash, all yield the same vinylic chloride:—



But certain compounds of ethylene yield paralactic acid, whilst the corresponding compounds of ethylidene give lactic



Ethylidene, the isomer of ethylene, has not yet been isolated, unless the hydrocarbon C_2H_4 derived from the transformation of ethyl is this body. The constitutional formula of ethylidene is



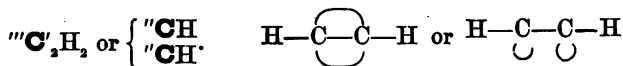
ACETYLENE or $\text{C}_n\text{H}_{2n-2}$ SERIES.

Acetylene is the radical belonging to this series which is best known. The series comprises the following members:—

| | |
|------------------|--------------------------|
| Acetylene..... | C_2H_2 . |
| Allylene | C_3H_4 . |
| Crotonylene..... | C_4H_6 . |
| Valerylene | C_5H_8 . |

These radicals stand in the same relation to the alcohols of the vinylic series as ethylene bears to ethylic alcohol. They are also probably capable of assuming tetrad functions.

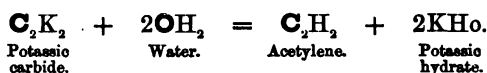
ACETYLENE.



Molecular weight = 26. *Molecular volume* $\square\square$. 1 litre weighs 13 criths.

Preparation.—1. By synthesis from its elements. . When an electric arc from a moderately powerful voltaic battery passes between carbon poles in an atmosphere of hydrogen, acetylene is produced.

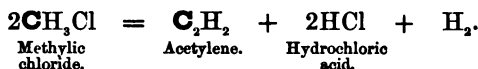
2. By the action of water on potassic carbide:—



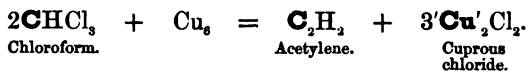
3. By the action of heat upon olefant gas or the vapour of alcohol, ether, or wood-spirit, or by passing electric sparks through marsh-gas:—



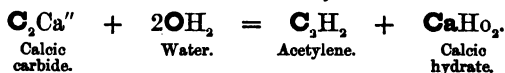
4. By heating the vapour of methylic chloride to low redness:—



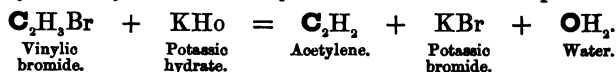
5. By passing the vapour of chloroform over ignited copper:—



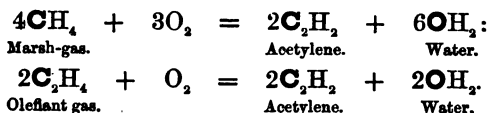
6. By the action of calcic carbide upon water:—



7. From vinylic bromide, one of the derivatives of ethylene, acetylene may be obtained by the action of alcoholic potash:—

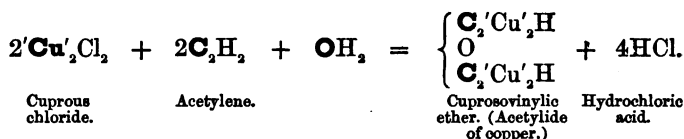
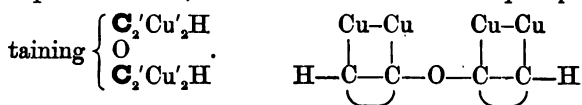


8. By the incomplete combustion of bodies containing carbon and hydrogen:—

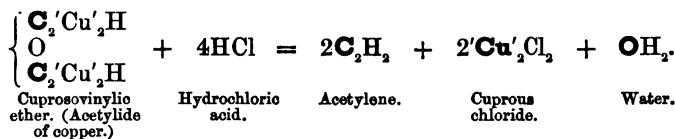


The crude acetylene, obtained by any of these processes, is

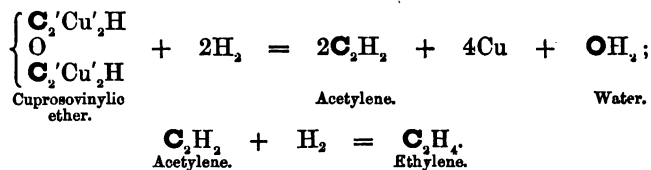
best purified by passing it through an ammoniacal solution of cuprous chloride, with which it forms a red precipitate con-



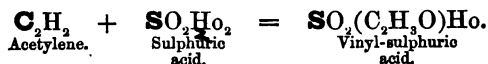
If ethylene has been present in the crude acetylene, the liquid containing the red precipitate is next heated to boiling, in order to decompose a compound which ethylene forms with copper. The cuprosovinyllic ether is then collected upon a filter and washed. On heating cuprosovinyllic ether with hydrochloric acid, pure acetylene is evolved:—



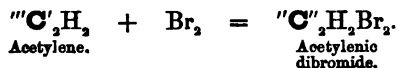
Reactions.—1. When cuprosovinyllic ether is heated with zinc and dilute ammonia, the nascent hydrogen, evolved by the action of the zinc upon the ammonia, unites with acetylene, producing ethylene:—



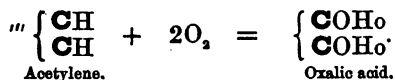
2. Acetylene is absorbed by sulphuric acid, producing vinyl-sulphuric acid:—



3. Acetylene unites with bromine, forming acetylenic dibromide :—



4. By agitating acetylene with solution of potassic permanganate, oxalic acid is formed :—



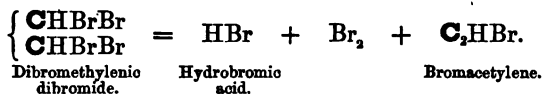
Carbonic anhydride and ormic acid are simultaneously produced :—



BROMACETYLENE.



By boiling together dibromethylenic dibromide with alcoholic potash, a spontaneously inflammable gas is evolved, which is bromacetylene.



PHENYLENE or $\text{C}_n\text{H}_{2n-6}$ SERIES.

The dyad radicals of this series are very little known.

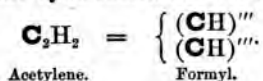
The following have alone been isolated :—

Phenylene, C_6H_4 .

Toluylene or Stilbene, C_7H_8 .

*POSITIVE RADICALS.***TRIADS.**

These radicals are unknown in the separate state, unless they are identical with the dyad radicals of the acetylene series:—



They are, however, well known in a numerous class of compounds belonging to families which will be studied hereafter.

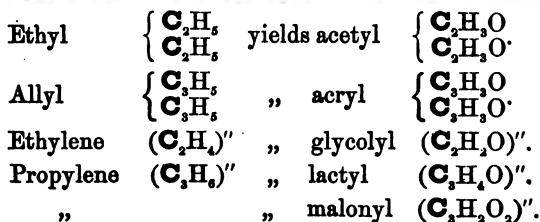
CHAPTER IV.

ORGANIC RADICALS.

CLASS II.

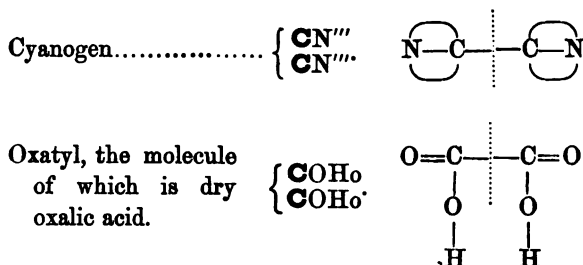
NEGATIVE RADICALS.

Every positive radical may be looked upon as the source of a negative radical, which is generated by displacing a portion of the hydrogen of the former by oxygen. Thus:—



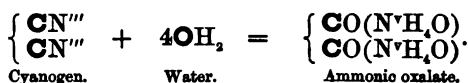
The constitution of the so-called compounds of these negative radicals may, however, be more simply explained from another point of view; and, in fact it will rarely be necessary for us to

recognize the existence of more than two negative radicals, in order to understand the whole range of negative organic compounds. These are:—

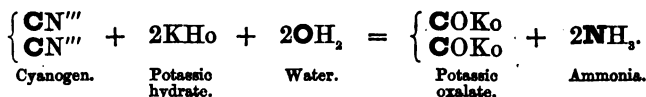


These two radicals are the acidifying principles of nearly all organic acids; they are, therefore, highly important compounds. The semimolecule of each consists of an atom of carbon, one bond of which is free to combine with other elements or groups of elements, the other three bonds being saturated, in cyanogen by triad nitrogen, and in oxatyl by one atom of oxygen and one semimolecule of hydroxyl. In the molecules of both, the two free bonds of the carbon saturate each other.

These radicals are closely related to each other. Thus, if cyanogen be dissolved in water, it is soon transformed into ammoniac oxalate:—

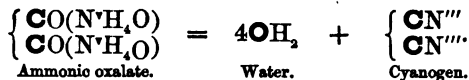


In the presence of potassic hydrate, cyanogen evolves ammonia and produces potassic oxalate:—

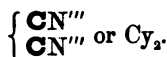


From these salts, oxalic acid, or the molecule of oxatyl, may be readily obtained by the action of sulphuric acid.

In the converse manner, oxatyl may be converted into cyanogen, by transforming it into ammonic oxalate and submitting this salt to the action of heat:—



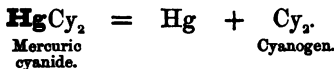
CYANOGEN.



Molecular weight = 52. *Molecular volume* $\square\square$. 1 litre weighs 26 criths. *Fuses at* -34° . *Boils at* $-20^\circ\cdot 7$.

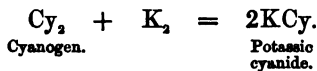
Occurrence.—Amongst the gases of blast furnaces,—a proof of its withstanding an extremely high temperature.

Preparation.—By the action of heat on mercuric cyanide:—

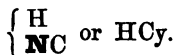


This equation only partially expresses the reaction, as a brown non-volatile compound (paracyanogen), Cy_n , is simultaneously produced.

Reaction.—Cyanogen unites directly with potassium:—

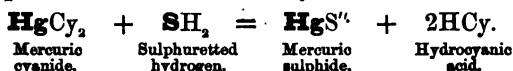


HYDROCYANIC ACID.

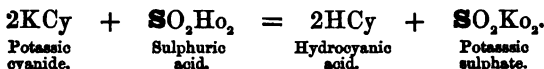


Molecular weight = 27. *Molecular volume* $\square\square$. 1 litre of hydrocyanic acid vapour weighs 13·5 criths. *Sp. gr. of liquid* 0·7058. *Fuses at* -15° . *Boils at* $26^\circ\cdot 5$.

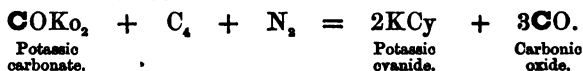
Preparation.—1. In the anhydrous condition, by passing hydrosulphuric acid over mercuric cyanide :—



2. By distilling potassic cyanide, or ferrocyanide, with dilute sulphuric acid :—

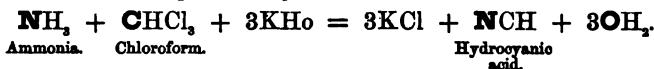


3. By passing nitrogen over an ignited mixture of potassic carbonate and carbon :—

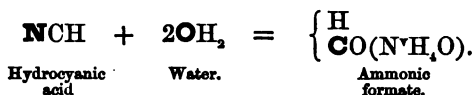


The potassic cyanide thus formed is then treated according to process No. 2.

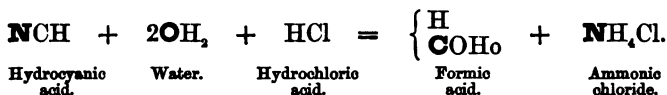
4. By heating together an alcoholic solution of ammonia, chloroform, and potassic hydrate :—



Reactions.—1. Hydrocyanic acid in contact with water slowly passes, partly into ammonic oxalate as mentioned at p. 26, and partly into ammonic formate :—



2. If hydrocyanic acid be mixed with concentrated hydrochloric acid, formic acid and ammonic chloride are produced :—



3. The displacement of the hydrogen in hydrocyanic acid by metals gives rise to a very extensive series of single and double cyanides. The following is a list of the most important of these compounds :—

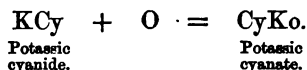
Single Cyanides.

| | |
|-------------------------|-------------------------------------|
| Potassic cyanide..... | KCy. |
| Zincic cyanide | ZnCy ₂ . |
| Cadmic cyanide | CdCy ₂ . |
| Nickelous cyanide | NiCy ₂ . |
| Argenticyanide | AgCy. |
| Mercuric cyanide | HgCy ₂ . |
| Aurous cyanide | AuCy. |
| Cuprous cyanide | 'Cu' ₂ Cy ₂ . |
| Ferrous cyanide..... | FeCy ₂ . |
| Cobaltous cyanide | CoCy ₂ . |

Double Cyanides.

| | |
|---|---|
| Dipotassic zincic tetracyanide | K ₂ Zn'', Cy ₄ . |
| Dipotassic cadmic tetracyanide | K ₂ Cd'', Cy ₄ . |
| Dipotassic nickelous tetracyanide | K ₂ Ni'', Cy ₄ . |
| Potassic argentic dicyanide | KAg, Cy ₂ . |
| Potassic aurous dicyanide..... | KAu, Cy ₂ . |
| Potassic auric tetracyanide | KAu''', Cy ₄ . |
| Dipotassic cuprous tetracyanide | K ₂ 'Cu'', Cy ₄ . |
| Dipotasssic platinous tetracyanide | K ₂ Pt'', Cy ₄ . |
| Tetrapotassic diplatinic decacyanide | K ₄ 'Pt''' ₂ Cy ₁₀ . |
| Tetrapotassic ferrous hexacyanide. (Potassic ferrocyanide.) | K ₄ Fe''Cy ₆ . |
| Hexapotassic diferric dodecacyanide. (Potassic ferricyanide.) | K ₆ 'Fe''' ₂ Cy ₁₂ . |
| Hexapotassic dicobaltic dodecacyanide. (Potassic cobalticyanide.) | K ₆ 'Co''' ₂ Cy ₁₂ . |
| Hexapotassic dichromic dodecacyanide ... | K ₆ 'Cr''' ₂ Cy ₁₂ . |
| Hexapotassic dimanganic dodecacyanide... | K ₆ 'Mn''' ₂ Cy ₁₂ . |

The cyanides of the alkali metals when fused in contact with air, absorb oxygen, producing cyanates:—



Some of the single cyanides, as potassic cyanide, are readily

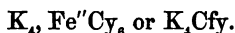
decomposed by acids; others, as ferrous and aurous cyanides, may be boiled with moderately strong acids without decomposition.

Most of the insoluble single cyanides dissolve in solutions of the alkaline cyanides, forming double cyanides. Some of these double compounds, when acted upon by hydrochloric acid, evolve hydrocyanic acid, producing chlorides of both metals, as in the case of dipotassic zinc tetracyanide. These are called *easily decomposable cyanides*, and are indicated in the above Table by the comma being placed between the cyanogen and the metals.

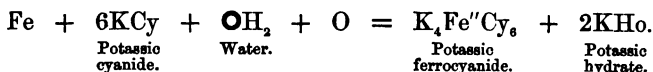
Other double cyanides do not evolve hydrocyanic acid under the influence of hydrochloric acid, but produce a chloride of one of the metals, the remaining elements of the compound uniting with hydrogen to form a complex acid. In the above Table the double cyanides of this class are indicated by the comma being placed between the metals.

The most important of these double cyanides are the potassic ferrocyanide $K_4Fe''Cy_6$, and the potassic ferricyanide $K_3Fe'''_2Cy_{12}$.

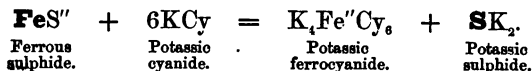
POTASSIC FERROCYANIDE.



Preparation.—1. By placing a mixture of iron filings and solution of potassic cyanide in contact with the air, oxygen is absorbed and potassic ferrocyanide produced:—



2. By digesting potassic cyanide with ferrous sulphide:—



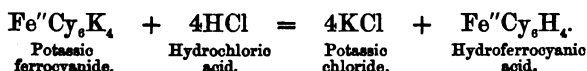
3. On a manufacturing scale it is prepared by fusing nitrogenous animal matter with potassic carbonate and iron filings in

iron vessels, lixiviating the resulting mass with water, and crystallizing.

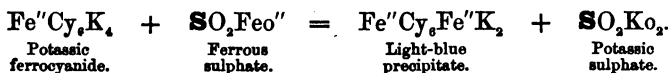
Reactions.—1. Potassic ferrocyanide, when fused with potassic carbonate, forms potassic cyanide and cyanate:—



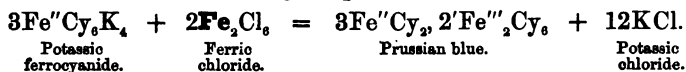
2. By mixing solution of potassic ferrocyanide with ether and hydrochloric acid, hydroferrocyanic acid is precipitated:—



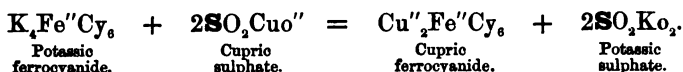
3. Potassic ferrocyanide produces, with solutions of ferrous salts, a light-blue precipitate, which rapidly becomes dark blue in contact with the air:—



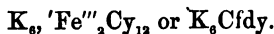
4. With ferric salts it gives prussian blue:—



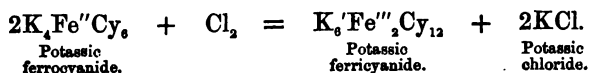
5. With cupric salts it gives a red precipitate of cupric ferrocyanide:—



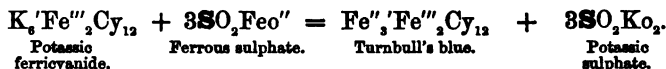
POTASSIC FERRICYANIDE.



Preparation.—By the action of oxidizing substances, such as chlorine or nitric acid, on potassic ferrocyanide:—



Reaction.—Potassic ferricyanide produces no precipitate with solutions of ferric salts, but causes a deep-blue precipitate with ferrous compounds :—



OTHER COMPOUNDS OF CYANOGEN.

There are three isomeric chlorides of cyanogen :—



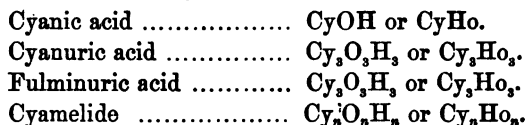
The molecular volume of all three cyanic chlorides is $\square\square$.

1 litre of gaseous cyanic chloride weighs 30.75 criths.

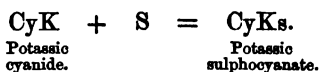
1 litre of vapour of liquid cyanic chloride weighs... 61.5 "

1 litre of vapour of solid cyanic chloride weighs ... 92.25 "

Cyanogen produces, with hydroxyl, three isomeric acids and an isomeric neutral body :—



When potassic cyanide is boiled with sulphur, the latter is dissolved and the solution contains potassic sulphocyanate :—



This compound produces with ferric salts a blood-red colour.

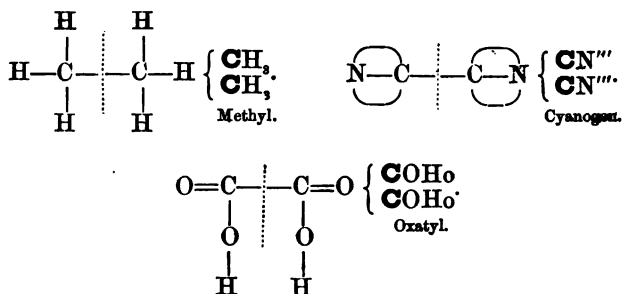
OXATYL.



This radical, in the isolated condition, constitutes dry oxalic

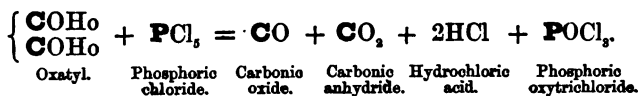
acid ; and in combination with hydrogen and other radicals it enters into the composition of nearly all organic acids. Acids containing one semimolecule of oxatyl are monobasic, those containing two are dibasic, and those containing three are tribasic.

The relations between methyl, oxatyl, and cyanogen are very simple :—

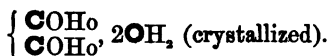


In methyl the two carbon atoms are united together by one bond of each, the remaining three bonds of each atom being saturated by three atoms of hydrogen. In cyanogen the carbon atoms are united in the same manner, but the three remaining bonds of each carbon atom are saturated by triad nitrogen; whilst in oxatyl the three remaining bonds are saturated with the dyad element oxygen and the monad radical hydroxyl.

Oxatyl has not been united with chlorine to produce oxatylic chloride (COHoCl); nor has its hydroxyl been replaced by chlorine to form $\left\{ \begin{array}{l} \text{COCl} \\ \text{COCl} \end{array} \right.$. When treated with phosphoric chloride, it yields carbonic oxide and carbonic anhydride :—



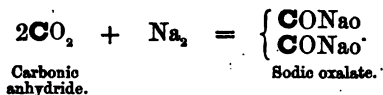
OXALIC ACID.



Occurrence.—In the form of the hydric potassic salt in *Oxalis acetosella*, and in the form of different salts in many other plants, and also in the animal organism.

Preparation.—1. From its elements through the medium of potassic cyanide. (See pp. 26 & 28.)

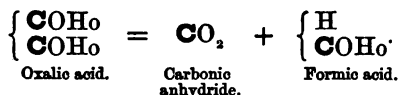
2. By passing carbonic anhydride over heated sodium:—



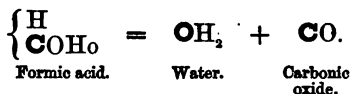
3. By the oxidation of a large number of organic compounds. Most organic substances are converted by oxidizing agents into oxalic acid before their final transformation into carbonic anhydride and water: thus sugar is transformed into oxalic acid by the action of nitric acid.

4. By heating sawdust with a mixture of potash and soda, oxalates of these bases are formed.

Transformations.—1. By the action of heat, oxalic acid is transformed into carbonic anhydride and oxalylic hydride, or formic acid:—

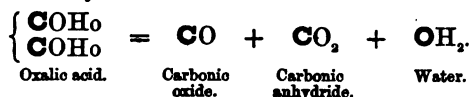


A portion of the formic acid is at the same time decomposed into water and carbonic oxide:—

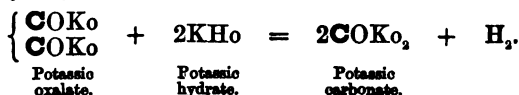


2. Substances having a strong attraction for water, such as sul-

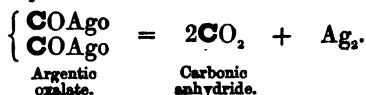
phuric acid, transform oxalic acid into water, carbonic oxide, and carbonic anhydride:—



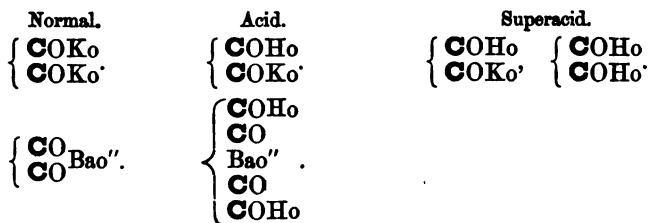
3. Heated with an excess of alkali, oxalic acid (or an oxalate) yields hydrogen and a carbonate:—



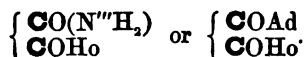
4. Argentic oxalate explodes when heated, producing silver and carbonic anhydride:—



Salts of Oxalic acid.—Oxalic acid forms three series of salts:—



OXAMIC ACID.

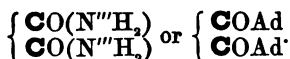


Preparation.—By heating hydric ammonic oxalate to 230°:—

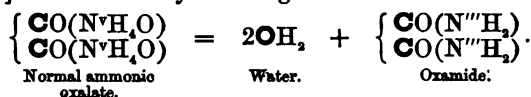


Reaction.—By boiling oxamic acid with water it is retransformed into hydric ammonic oxalate.

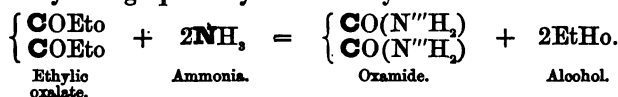
OXAMIDE.



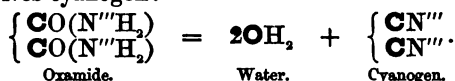
Preparation.—1. By distilling normal ammonic oxalate:—



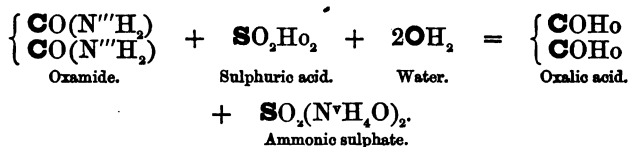
2. By acting upon ethylic oxalate by ammonia:—



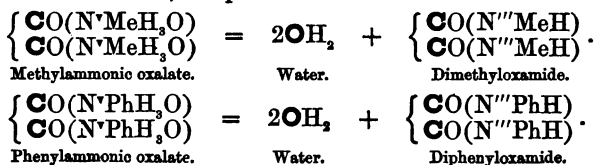
Reactions.—1. Oxamide, when heated with phosphoric anhydride, evolves cyanogen:—



2. Dilute acids convert it into oxalic acid and ammonic salts:—



By distilling the oxalates of the compound ammonias instead of ammonic oxalate, compound oxamides are obtained:—



CHAPTER V.

HYDRIDES OF THE ORGANIC RADICALS.

This family is divided into two classes :—

Class I. Hydrides of the Positive Radicals.

Class II. Hydrides of the Negative Radicals.

Class I.

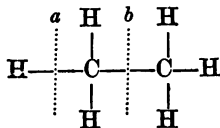
HYDRIDES OF THE POSITIVE RADICALS.

Two series of hydrides belonging to this class are well known ; they are :—

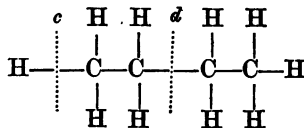
1. Hydrides of the Radicals of the Methyl series.
2. Hydrides of the Radicals of the Phenyl series.

1. *HYDRIDES OF THE RADICALS OF THE METHYL SERIES, Marsh-gas or C_nH_{2n+2} Series.*

There is some difference of opinion as to whether these compounds are identical or isomeric with the radicals of the methyl series. Thus methyl and ethylic hydride both contain C₂H₆, and ethyl and butylic hydride both contain C₄H₁₀. The graphic formulæ exhibit no difference between these pairs of bodies respectively. Thus :—



Methyl or ethylic hydride.



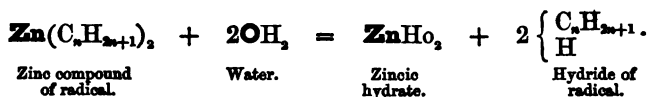
Ethyl or butylic hydride.

These formulæ do not show us whether the molecule of methyl or ethylic hydride will separate at *a* and so be represented by the formula $\begin{Bmatrix} \text{C}(\text{CH}_3)\text{H}_2 \\ \text{H} \end{Bmatrix}$, or at *b* and so be written thus,

$\left\{ \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \right.$; or whether the molecule of ethyl or butylic hydride will separate at *c*, and so be formulated $\left\{ \begin{smallmatrix} \text{C}(\text{C}_2\text{H}_5) \\ \text{H} \end{smallmatrix} \right. \text{H}_2$ —or at *d*, when it should be represented by $\left\{ \begin{smallmatrix} \text{C}(\text{CH}_3) \\ \text{C}(\text{CH}_3) \end{smallmatrix} \right. \text{H}_2$. Some experiments in connexion with this subject appear to show that these compounds are isomeric.

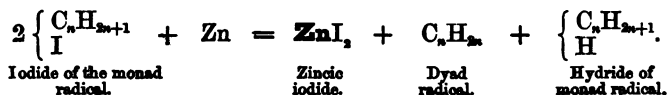
A difference between methyl and ethylic hydride can only be conceived on the supposition that the four bonds of carbon have not equal values in combination, an hypothesis which is not altogether unsupported by facts.

Preparation.—1. There is only one process of general application for preparing these hydrides; it consists in bringing water into contact with the zinc compounds of the respective radicals:—



The corresponding compounds containing more positive metals might doubtless be substituted for those of zinc.

2. There are several special processes which may be used for preparing these hydrides. Thus all the hydrides above that of methyl may be obtained, together with the corresponding dyad radical, by acting upon the iodide of the monad radical by zinc:—



Methylic hydride, or marsh-gas, is produced during putrefaction, and by the distillation of potassic acetate with excess of potassic hydrate.

The destructive distillation of coal and of allied substances also furnishes a large number of the members of this series.

Character.—They are all distinguished by their great chemical

indifference, and by their forming substitution compounds containing chlorine, bromine, &c.

The following list contains the hydrides of the monad radicals hitherto studied:—

| | | Boiling-points. |
|-------------------------------------|---------------------------------------|-------------------|
| Methylic hydride, or Marsh-gas..... | MeH or C H ₄ | |
| Ethylic hydride | EtH or C ₂ H ₆ | |
| Propylic or tritylic hydride | PrH or C ₃ H ₈ | |
| Butylic or tetrylic hydride | BuH or C ₄ H ₁₀ | slightly above 0° |
| Amylic or pentylic hydride | AyH or C ₅ H ₁₂ | 30° |
| Hexylic or caproylic hydride | CpH or C ₆ H ₁₄ | 68° |
| Heptylic hydride | C ₇ H ₁₆ | 92–94° |
| Octylic hydride | C ₈ H ₁₈ | 116–118° |
| Nonylic hydride..... | C ₉ H ₂₀ | 136–138° |
| Decatylic hydride | C ₁₀ H ₂₂ | 160–162° |
| Endecatylic hydride | C ₁₁ H ₂₄ | 180–184° |
| Dodecatylic hydride | C ₁₂ H ₂₆ | 196–200° |
| Tridecatylic hydride | C ₁₃ H ₂₈ | 216–218° |
| Tetradecatylic hydride | C ₁₄ H ₃₀ | 236–240° |
| Pentadecatylic hydride | C ₁₅ H ₃₂ | 255–260° |

METHYLIC HYDRIDE, Marsh-gas, Light Carburetted

Hydrogen, Fire-damp.

CH₄ or MeH.

Molecular weight = 16. *Molecular volume* $\square\square$. 1 litre weighs 8 criths.

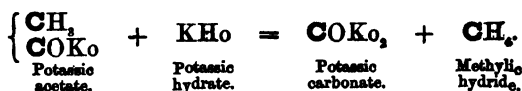
Occurrence.—1. As a product of the decomposition of organic substances out of contact with air.

2. Evolved in coal-mines.

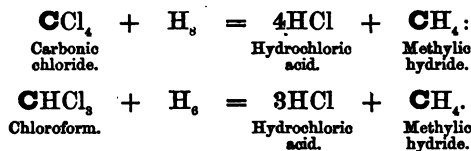
3. The gas of the mud-volcano at Bulganak in the Crimea is nearly pure marsh-gas.

Preparation.—1. By the action of water on zincic methide. (See general reaction, p. 38.)

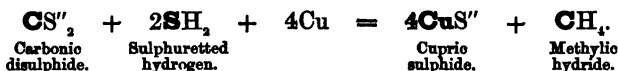
2. By distilling two parts of potassic acetate, two of potassic hydrate, and three of lime:—



3. By the reduction of carbonic chloride or of chloroform with sodium amalgam and water :—

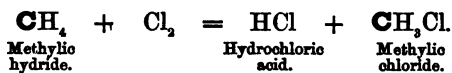


4. By passing carbonic disulphide and hydrosulphuric acid, or carbonic disulphide and steam, over ignited copper :—



5. By the destructive distillation of organic substances, such as wood and coal.

Reactions.—1. When equal volumes of methylic hydride and chlorine are exposed to diffused daylight, methylic chloride is formed :—



2. When methylic hydride is passed through a red-hot tube, hydrogen, ethylene, acetylene, and ethylic hydride are produced.

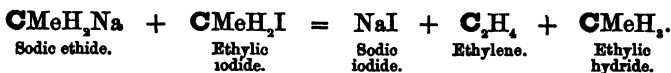
ETHYLIC HYDRIDE.



Molecular weight = 30. *Molecular volume* $\square\square$. 1 litre weighs 15 criths.

Preparation.—1. By the action of water on zincic ethide (see p. 38).

2. By the action of ethylic iodide on sodic ethide, ethylene being simultaneously produced :—

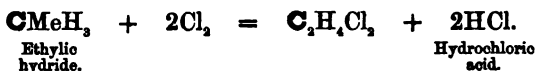


Reactions.—1. When equal volumes of ethylic hydride and chlorine are exposed to diffused daylight, the following action takes place :—



A small portion of the body CMeH_2Cl is ordinary ethylic chloride, which is a liquid, boiling at $12^\circ.5$; but the rest is a gas which does not condense at -18° .

2. When a mixture of two volumes of chlorine and one of ethylic hydride is exposed to the action of diffused daylight, an oily liquid having the composition of ethylenic dichloride is formed :—



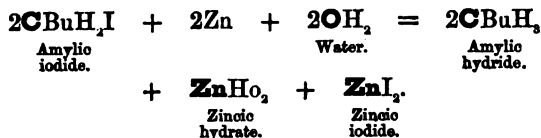
AMYLIC HYDRIDE.



Molecular weight = 72. *Molecular volume* $\square\square$. 1 litre of amylic hydride vapour weighs 36 criths. Boils at 30° .

Occurrence.—In petroleum and coal-oil.

Preparation.—By digesting zinc and amylic iodide with water or alcohol at 100° :—



PARAFFIN.



This body is produced, together with numerous other compounds of a like nature, by the destructive distillation of bog-

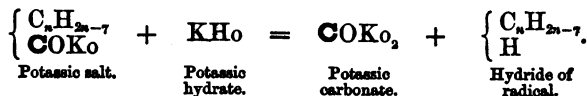
head coal and similar substances. It is also found in petroleum and asphalt. Chlorine has no action upon paraffin in the cold; but if it be passed into melted paraffin, the latter is slowly attacked, hydrochloric acid being evolved. In this reaction paraffin resembles the hydrides of the monad radicals, and differs from the dyad radicals, to which class it was formerly considered to belong. In the formula C_nH_{2n+2} for paraffin, the value of n has not yet been satisfactorily determined; in fact it is probable that several distinct hydrides of the class now under consideration are confounded under this name.

2. HYDRIDES OF THE RADICALS OF THE PHENYL SERIES.

The following six members of this series are known, viz. :—

| | Formulae. | Boiling-points. ° | Sp. gr. |
|--------------|----------------|----------------------|---------|
| Pentol..... | C_5H_4 | 60·0 | — |
| Benzol | C_6H_5 | 80·5 | 0·85 |
| Toluol..... | C_7H_8 | 110·0 | 0·87 |
| Xylol | C_8H_{10} | 128·5 | — |
| Cumol..... | C_9H_{12} | 148·5 | 0·87 |
| Cymol..... | $C_{10}H_{14}$ | 171·4 | 0·86 |

Preparation.—1. These hydrides are produced by the distillation of the alkaline salts of the acids containing the same positive radicals, with excess of potassic hydrate :—



2. By the destructive distillation of various organic substances, such as coal.

Methyl-phenyl, C_6H_5Me , is ordinary coal-tar toluol.

Ethyl-phenyl, C_6H_5Et , is not xylol from coal-tar; it boils at 135° , six or seven degrees above the boiling-point of coal-tar

xylol. Ethyl-phenyl produces a nitro-compound which can be distilled; it boils at 233°. Ethyl-phenyl, when oxidized by chromic acid, gives benzoic acid and carbonic anhydride, while xylol gives terephthalic acid.

Xylol from coal-tar is dimethyl-benzol or methyl-benzyl, $C_6H_4Me_2$. It may be produced by the action of bromotoluol upon methylic iodide in presence of sodium.

Diethyl-benzol, by oxidation with chromic acid, gives water, carbonic anhydride, and terephthalic acid:—



Oxidized with dilute nitric acid, it gives ethylbenzoic acid:—



Cymol from cumin oil and from camphor are isomeric.

Methyl-xylol or trimethyl-benzol, $C_6H_3Me_3$, is the cumol of tar. It boils at 165°–166°, and gives a compound with bromine fusing at 72°–73°.

Ethyl-xylol, dimethyl ethyl-benzol, $C_6H_3Me_2Et$, boils at 183°–184°, and by oxidation gives acetic acid and an acid resembling terephthalic.

Properties.—These hydrides are distinguished from those of the radicals of the C_nH_{2n+1} series by being less indifferent to chemical agents. By treatment with strong nitric acid they yield nitro-compounds:—

Thus Pentol, C_5H_{11} , gives nitropentol, $C_5H_9(N^oO_2)$?

„ Benzol, C_6H_6 , „ nitrobenzol, $C_6H_5(N^oO_2)$.

„ Toluol, C_7H_8 , „ nitrotoluol, $C_7H_7(N^oO_2)$.

„ Xylol, C_8H_{10} , „ nitroxylol, $C_8H_9(N^oO_2)$.

„ Cumol, C_9H_{12} , „ nitrocumol, $C_9H_{11}(N^oO_2)$.

„ Cymol, $C_{10}H_{14}$, „ nitrocymol, $C_{10}H_{13}(N^oO_2)$.

Under the influence of reducing agents, these nitro-compounds yield aniline and its homologues.

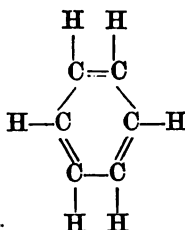
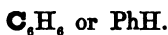
Pure nitrotoluol is solid at ordinary temperatures. It boils

at 237°. By reduction it gives toluidine; and by the action of potassic chromate and sulphuric acid, paranitrobenzoic acid or nitrodraçylic acid is formed.

So-called liquid nitrotoluol is a mixture of nitrobenzol and nitrotoluol.

BENZOL, Benzene, Benzine, Phenylc Hydride,

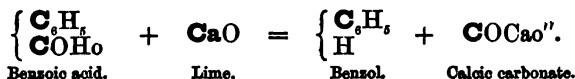
Bicarburet of Hydrogen.



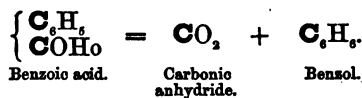
Molecular weight = 78. *Molecular volume* $\square\square$. 1 litre of benzol-vapour weighs 39 criths. *Fuses* at 5°.5. *Boils* at 80°.5.

Occurrence.—In Rangoon petroleum and in coal-tar.

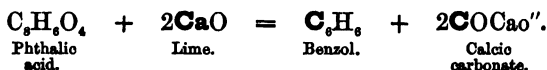
Preparation.—1. By heating benzoic acid with excess of lime or baryta :—



2. By heating the vapour of benzoic acid to redness, when it splits into benzol and carbonic anhydride :—



3. By heating phthalic acid with lime:—



4. By passing fats through red-hot tubes.

5. By the destructive distillation of coal.

6. In small quantity, when the vapour of acetic acid or of alcohol is passed through a red-hot tube.

SUBSTITUTION DERIVATIVES OF BENZOL.

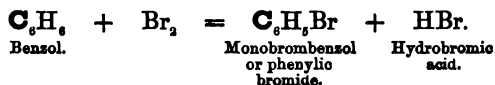
I. Bromo-Compounds.

MONOBROMBENZOL.

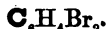


Boils at 150°.

Preparation.—By acting with two atoms of bromine on boiling benzol:—



DIBROMBENZOL.



Fuses at 89°. Boils at 219°.

Preparation.—By treating monobrombenzol with excess of bromine.

TRIBROMBENZOL HYDROBROMATE.

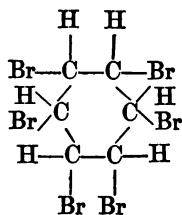
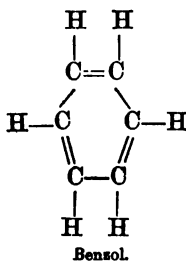


Preparation.—By exposing a mixture of benzol and bromine to the action of sunlight.

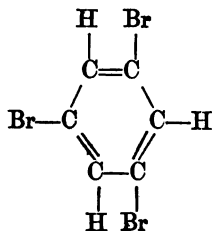
TRIBROMBENZOL.

Preparation.—By boiling the previous compound with alcoholic potash.

The following graphic formulæ show the probable atomic relations subsisting between benzol, tribrombenzol hydrobromate, and tribrombenzol:—



Tribrombenzol hydrobromate.



Tribrombenzol.

II. *Chloro-compounds.*

Benzol forms three chloro- substitution compounds, similar to the bromo-compounds just described.

| | State of aggregation. | Fusing-point. | Boiling-point. | Sp. gr. |
|--|-----------------------|---------------|----------------|---------|
| Monochlorbenzol ... $\text{C}_6\text{H}_5\text{Cl}$, | Liquid... | — | 136°. | — |
| Dichlorbenzol $\text{C}_6\text{H}_4\text{Cl}_2$, | Solid ... | 89°. | — | — |
| Trichlorbenzol $\text{C}_6\text{H}_3\text{Cl}_3$, | Oily ... | — | 210° | 1.457. |

III. *Nitro-compounds.*

Two only have hitherto been produced:—

Nitrobenzol $\text{C}_6\text{H}_5(\text{N}^\circ\text{O}_2)$ or $\text{N}(\text{C}_6\text{H}_5)\text{O}_2$.

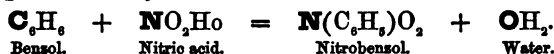
Dinitrobenzol $\text{C}_6\text{H}_4(\text{N}^\circ\text{O}_2)_2$ or $\text{N}_2(\text{C}_6\text{H}_4)^\circ\text{O}_2$.

NITROBENZOL.

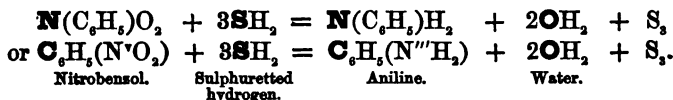
$\text{N}(\text{C}_6\text{H}_5)\text{O}_2$ or NPhO_2 .

Molecular weight = 123. *Molecular volume* $\square\square$. 1 litre of nitrobenzol vapour weighs 61.5 criths. *Fuses at* 3°. *Boils at* 220°.

Preparation.—By the action of nitric acid on benzol:—

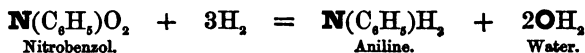


Reactions.—1. By the action of reducing or hydrogenating agents, as zinc and hydrochloric acid, sulphuretted hydrogen, acetic acid and iron, or potassic arsenite, nitrobenzol is converted into aniline:—

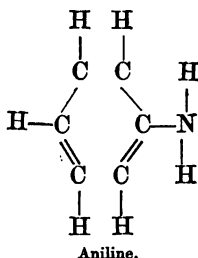
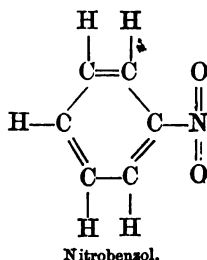


2. Nitrobenzol is also converted into aniline when its

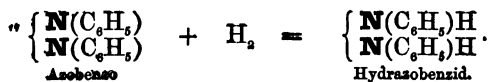
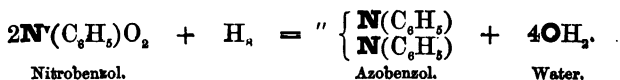
vapour, mixed with hydrogen, is passed over spongy palladium:—



The relation between nitrobenzol and aniline will be seen in the following graphic formulæ:—



3. By the action of sodium amalgam and water, nitrobenzol is converted into azobenzol, and finally into hydrazobenzid:—



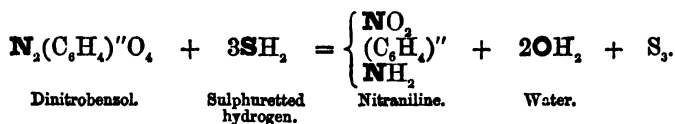
DINITROBENZOL.



Fuses below 100°.

Preparation.—By treating nitrobenzol with a mixture of concentrated nitric and sulphuric acids.

Reaction.—By the action of sulphuretted hydrogen, dinitrobenzol is converted into nitraniline:—



CLASS II.

HYDRIDES OF NEGATIVE RADICALS.

Only two of these are known:—

Cyanic hydride or Hydrocyanic acid.

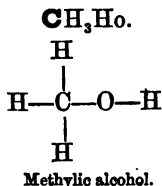
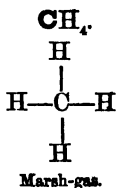
Oxalylic hydride or Formic acid.

The first has already been considered (p. 27) ; and the second will be more conveniently studied in connexion with the fatty acids (p. 121).

CHAPTER VI.

THE ALCOHOLS.

THE alcohols form one of the most important of the families of organic compounds. The simplest member of this family is methylic alcohol, which is derived from marsh-gas by the substitution of one semimolecule of hydroxyl for one of hydrogen.

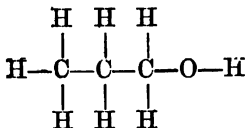


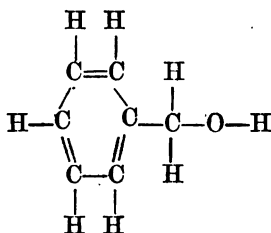
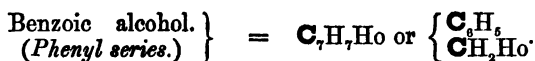
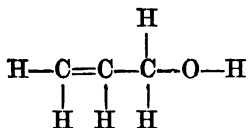
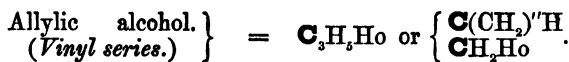
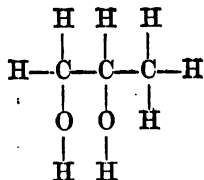
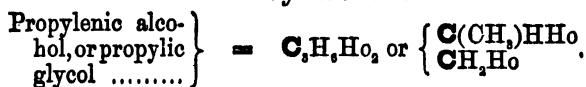
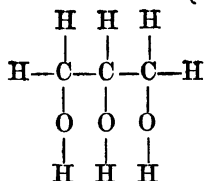
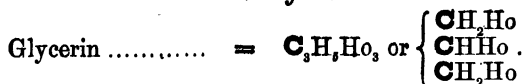
The alcohols have been termed the hydrated oxides of the positive radicals; but this is erroneous, as they do not contain water. They may more correctly be defined as the compounds of hydroxyl with the positive organic radicals, whence it follows that each series of positive radicals forms a corresponding series of alcohols. The alcohols act upon and saturate acids, forming a family of compounds termed *ethereal salts*. The acidity or acid-saturating power of the alcohols depends upon the number of semimolecules of hydroxyl which they contain: the monad radicals give monohydric alcohols, or alcohols containing only one semimolecule of hydroxyl, the dyad radicals dihydric alcohols, &c. We have thus the annexed three principal subdivisions of the alcohol family.

| Monohydric. | Dihydric. | Trihydric. |
|---|--|---|
| Methyl or $\text{C}_n\text{H}_{2n+1}\text{Ho}$ series. | Glycol or $\text{C}_n\text{H}_{2n}\text{Ho}_2$ series. | Glycerin or $\text{C}_n\text{H}_{2n-1}\text{Ho}_3$ series. |
| Vinyl or $\text{C}_n\text{H}_{2n-1}\text{Ho}$ series. | Orcin or $\text{C}_n\text{H}_{2n-2}\text{Ho}_2$ series. | Pyrogallie or $\text{C}_n\text{H}_{2n-3}\text{Ho}_3$ series. |
| Phenyl or $\text{C}_n\text{H}_{2n-7}\text{Ho}$ series. | | |

The following symbolic and graphic formulæ will exemplify the disposal of the bonds in these three subdivisions:—

Monohydric Alcohols.



*Dihydric Alcohols.**Trihydric Alcohols.*

*MONOHYDRIC ALCOHOLS:*Methyl or $C_nH_{2n+1}Ho$ series.

These alcohols may be divided into three classes, viz.:—

1. Monohydric normal alcohols $\left\{ \begin{array}{l} C(C_nH_{2n+1})H_2 \\ CH_2Ho \end{array} \right.$
2. " secondary " $\left\{ \begin{array}{l} C(C_nH_{2n+1})H_2 \\ C(C_mH_{2m+1})HHo \end{array} \right.$
3. " tertiary " $\left\{ \begin{array}{l} C(C_nH_{2n+1})H_2 \\ C(C_mH_{2m+1})_2Ho \end{array} \right.$

In the general formula of the normal alcohols n may = 0, and even the whole radical $C(C_nH_{2n+1})H_2$ may be replaced by hydrogen, as is the case in methylic alcohol. In the formulæ of the secondary and tertiary alcohols n may also = 0, but m must always be a positive integer.

*NORMAL MONOHYDRIC ALCOHOLS.*General formula $\left\{ \begin{array}{l} C(C_nH_{2n+1})H_2 \\ CH_2Ho \end{array} \right.$

The following is a list of the members of this class:—

| | | Fusing- points. | Boiling- points. |
|---|--|--------------------|---------------------|
| Methylic alcohol | $\left\{ \begin{array}{l} H \\ CH_2Ho \end{array} \right.$ | — | 66°·5. |
| Ethylic alcohol | $\left\{ \begin{array}{l} CH_3 \\ CH_2Ho \end{array} \right.$ | — | 78°·4. |
| Propylic or tritylic al- cohol | $\left\{ \begin{array}{l} CMeH_2 \\ CH_2Ho \end{array} \right.$ or $\left\{ \begin{array}{l} C(CH_3)H_2 \\ CH_2Ho \end{array} \right.$ | — | 97°. |
| Butylic or tetrylic al- cohol | $\left\{ \begin{array}{l} CEtH_2 \\ CH_2Ho \end{array} \right.$ or $\left\{ \begin{array}{l} C(C_2H_5)H_2 \\ CH_2Ho \end{array} \right.$ | — | 115°. |
| Isobutylic alcohol | $\left\{ \begin{array}{l} CMe_2H \\ CH_2Ho \end{array} \right.$ or $\left\{ \begin{array}{l} C(CH_3)_2H \\ CH_2Ho \end{array} \right.$ | — | 109°. |
| Amylic or pentylic al- cohol | $\left\{ \begin{array}{l} CPrH_2 \\ CH_2Ho \end{array} \right.$ or $\left\{ \begin{array}{l} C(C_3H_7)H_2 \\ CH_2Ho \end{array} \right.$ | — | 137°. |
| Isamylic alcohol | $\left\{ \begin{array}{l} CPr_2H_2 \\ CH_2Ho \end{array} \right.$ or $\left\{ \begin{array}{l} C(CMe_2H)H_2 \\ CH_2Ho \end{array} \right.$ | -20°. | 129°. |
| Pseudamylic alcohol ... | $\left\{ \begin{array}{l} CEtMeH \\ CH_2Ho \end{array} \right.$ or $\left\{ \begin{array}{l} C(C_2H_5)(CH_3)H \\ CH_2Ho \end{array} \right.$ | — | 128°. |
| Caproylic or hexylic alcohol | $\left\{ \begin{array}{l} C_6H_{11} \\ CH_2Ho \end{array} \right.$ | — | 150°. |

| | | Fusing- points. | Boiling- points. |
|-------------------------------------|---|--------------------|---------------------|
| Enanthylic or heptylic alcohol..... | $\left\{ \begin{array}{l} \text{C}_7\text{H}_{13} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | — | 170°. |
| Caprylic or octylic alcohol | $\left\{ \begin{array}{l} \text{C}_8\text{H}_{17} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | — | 190°. |
| Nonylic alcohol | $\left\{ \begin{array}{l} \text{C}_9\text{H}_{19} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | — | 200°. |
| Decatylic alcohol..... | $\left\{ \begin{array}{l} \text{C}_{10}\text{H}_{21} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | — | 212°. |
| Cetylic alcohol | $\left\{ \begin{array}{l} \text{C}_{15}\text{H}_{31} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | 50°. | — |
| Cerotic alcohol | $\left\{ \begin{array}{l} \text{C}_{26}\text{H}_{53} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | 79°. | — |
| Melissic alcohol | $\left\{ \begin{array}{l} \text{C}_{29}\text{H}_{59} \\ \text{CH}_2\text{Ho} \end{array} \right.$ | 85°. | — |

The lower members of the class are liquid, and the higher solid. They are produced in a variety of operations, such as destructive distillation, fermentation, and animal secretion, but by reactions which cannot usually be traced.

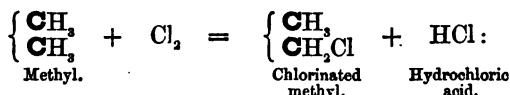
Relations of the normal $\text{C}_n\text{H}_{2n+1}\text{Ho}$ alcohols to the monad $\text{C}_n\text{H}_{2n+1}$ radicals.

1. The radicals $\text{C}_n\text{H}_{2n+1}$ which are combined with hydroxyl in the normal alcohols may be separated, by first converting the alcohol into an iodide (see p. 96), and subsequently acting on the iodide by zinc (see p. 11).

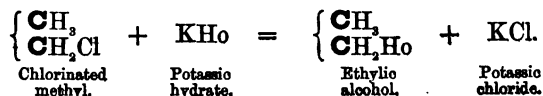
2. The radical next lower in the series, than that contained in the alcohol, may be obtained by converting the alcohol into the corresponding fatty acid, and then submitting a salt of this acid to electrolysis (see p. 119).

3. Inversely, the normal alcohols may be obtained by acting upon the normal radicals with chlorine under the influence of light, when one atom of hydrogen in the radical is displaced by chlorine.

Thus in the case of methyl we have



by the action of potassic hydrate upon this chlorinated methyl, ethylic alcohol is formed, thus:—



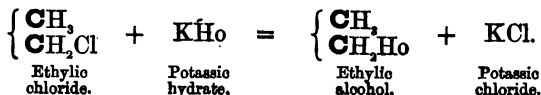
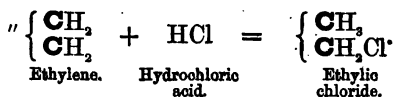
This reaction requires further investigation (see p. 55).

Relations of the normal $\text{C}_n\text{H}_{2n+1}\text{Ho}$ alcohols to the dyad C_nH_{2n} radicals.

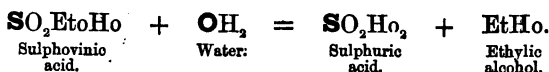
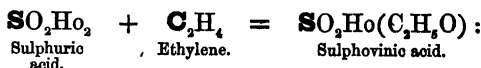
1. The C_nH_{2n} radicals are obtained from the normal $\text{C}_n\text{H}_{2n+1}\text{Ho}$ alcohols by the abstraction of the elements of water:—



2. Inversely, the normal alcohols are obtained from these radicals by first uniting the latter with hydrochloric, hydrobromic, or hydriodic acid, and then treating the product with potassic hydrate:—



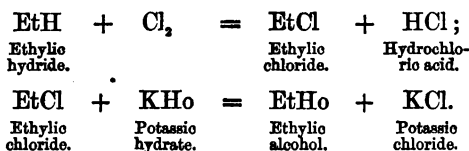
Or by uniting the dyad radicals with sulphuric acid, and distilling the product with water:—



*Relations of the normal $C_nH_{2n+1}Ho$ alcohols to the hydrides
of the C_nH_{2n+1} radicals.*

1. When the alcohols are converted into iodides (see p. 96) and the latter digested with zinc and water at 100° , the corresponding hydrides are produced (see p. 88).

2. When the hydrides of the C_nH_{2n+1} radicals are acted upon by chlorine under the influence of light, they produce the chlorides of the radicals, from which the alcohols may be obtained by the action of potassic hydrate:—

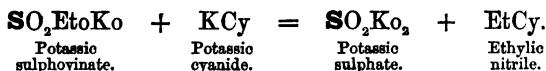


The greater quantity of the chlorine compound so formed is isomeric with the chloride of the radical, and possibly gives a corresponding isomeric alcohol.

Relations of the $C_nH_{2n+1}Ho$ alcohols to the radical cyanogen.

Ascent of the alcohol series. Mendius's reaction.

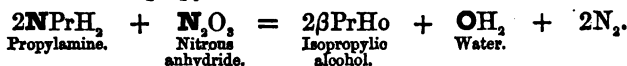
By the dry distillation of potassic sulphovinate and its homologues with potassic cyanide, the nitriles or abnormal cyanides of the radicals are produced:—



By treatment with nascent hydrogen, this ethylic nitrile is converted into propylamine:—

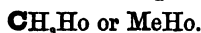


By the action of nitrous anhydride, propylamine is transformed into isopropylic alcohol :—



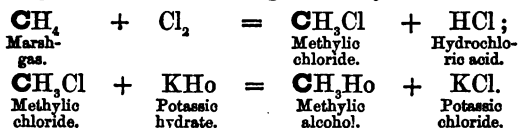
It is obvious that by repeating these reactions on isopropylic alcohol, butylic alcohol would be obtained, the homologous series of alcohols being ascended one step at each repetition of the process. But the alcohols are, if possible, secondary or tertiary.

METHYLIC ALCOHOL, *Wood Spirit*, *Pyroxylic Spirit*.

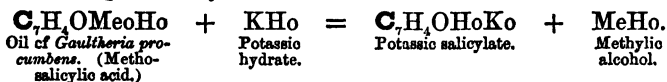


Molecular weight = 32. *Molecular volume* $\square\square$. 1 litre of methylic alcohol vapour weighs 16 criths. *Sp. gr.* 0.798. *Boils at* 66°5.

Preparation.—1. From marsh-gas, by the action of chlorine and subsequent treatment with potassic hydrate :—

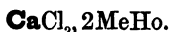


2. From the essential oil of *Gaultheria procumbens*, by the action of potassic hydrate :—



3. By the destructive distillation of wood.

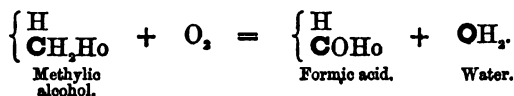
Reactions.—1. Methylic alcohol unites with some salts in the capacity of water of crystallization, as, for instance,—



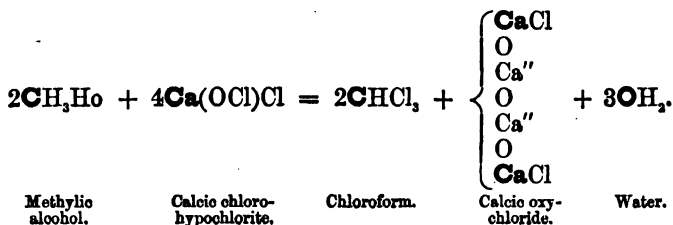
2. By the action of potassium and sodium, methylates are formed with elimination of hydrogen :—



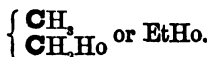
3. By oxidation it is transformed into formic acid:—



4. When distilled with calcic chloro-hypochlorite (*chloride of lime*) and water, chloroform is produced.



ETHYLIC ALCOHOL, *Alcohol, Spirit of Wine.*



Molecular weight = 46. *Molecular volume* $\square\square$. 1 litre of ethylic alcohol vapour weighs 23 criths. *Sp. gr.* 0.792 at 20°. *Boils* at 78°4.

Preparation.—1. From ethylene (p. 54).

2. By the fermentation of grape-sugar with yeast at a temperature of about 22°:—

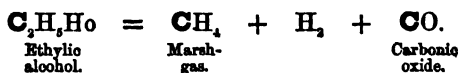


At the same time, however, other products are formed, but in very small quantities.

Reactions.—1. Treated with potassium or sodium, alcohol forms ethylates:—

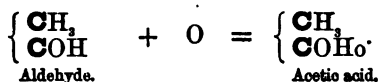
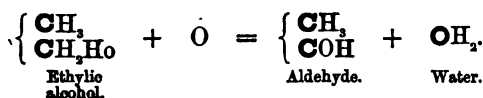


2. When passed through a red-hot tube, alcohol is decomposed into marsh-gas, hydrogen, and carbonic oxide:—



Small quantities of ethylene, benzol, and naphthalin are simultaneously produced, whilst carbon is deposited.

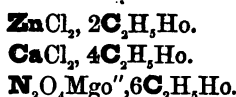
3. By oxidation, ethylic alcohol is converted first into aldehyde, and then into acetic acid:—



4. Distilled with chloride of lime, ethylic alcohol produces chloroform.

Alcoholates are salts containing alcohol in the place of water of crystallization; they are mostly decomposed immediately by water.

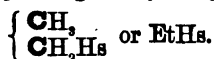
The following are known:—



5. Treated with chlorine as long as hydrochloric acid is evolved, it is transformed into ethylic chloride and chloral hydrate (the aldehyde of trichloroacetic acid):—

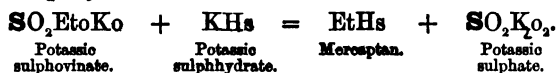


MERCAPTAN, *Sulphur Alcohol, Ethylic sulphhydrate, Hydrosulphate of Ethyl.*



Molecular weight = 62. *Molecular volume* $\square\square$. 1 litre of mercaptan vapour weighs 31 criths. *Sp. gr. of liquid* 0.835. *Boils at* 63°.

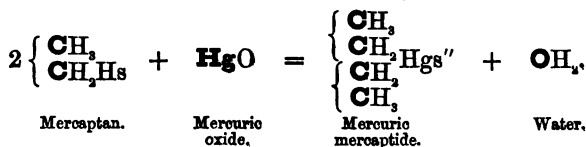
Preparation.—By distilling potassic sulphovinate with potassic sulphhydrate:—



Reactions.—1. By the action of potassium and sodium on mercaptan, an atom of hydrogen is displaced by the metal, producing mercaptides:—



2. Mercaptan acts upon mercuric oxide with great energy, a white crystalline mercuric mercaptide being formed:—



Propylic alcohol, $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{CH}_2\text{Ho} \end{array} \right.$, is obtained from the fusel oil of the marc brandy of the south of France.

Butylic alcohol, $\left\{ \begin{array}{l} \text{CMe}_2\text{H} \\ \text{CH}_2\text{Ho} \end{array} \right.$, is contained in the fusel oil produced in the preparation of spirit from the molasses of beet-root sugar. Butylic alcohol of the form $\left\{ \begin{array}{l} \text{CEtH}_2 \\ \text{CH}_2\text{Ho} \end{array} \right.$ is obtained from butylic acid by Piria and Wurtz's reactions, described at p. 120.

Amylic alcohol, $\left\{ \begin{array}{l} \text{CPr}\beta\text{H}_2 \\ \text{CH}_2\text{H}_o \end{array} \right.$, is the chief constituent of the fusel oil obtained in the manufacture of alcohol from potatoes or grain. Two other normal, isomeric amylic alcohols are given in the Table at p. 52.

As far as these alcohols have been studied, they resemble, in their chemical relations, the two previously described.

SECONDARY MONOHYDRIC ALCOHOLS.

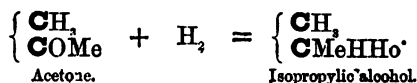
General formula... $\left\{ \begin{array}{l} \text{C}(\text{C}_n\text{H}_{2n+1})\text{H}_2 \\ \text{C}(\text{C}_m\text{H}_{2m+1})\text{HH}_o \end{array} \right.$

The secondary alcohols differ from the normal in yielding, by oxidation, ketones instead of acids.

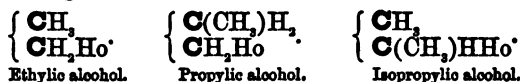
Seven secondary alcohols are at present known:—

| | Boiling- points, ° |
|--|---|
| Isopropyl alcohol or dimethyl carbinol | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CMeHH}_o \end{array} \right.$ 84. |
| Methylethyl carbinol | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CEtHH}_o \end{array} \right.$ 97. |
| Methylpropyl carbinol | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CPrHH}_o \end{array} \right.$ 122. |
| Methylisopropyl carbinol ... | $\left\{ \begin{array}{l} \text{CMe}_2\text{H} \\ \text{CMeHH}_o \end{array} \right.$ 106. |
| Pseudoheptylic alcohol or methylbutyl carbinol | $\left\{ \begin{array}{l} \text{CPrH}_2 \\ \text{CMeHH}_o \end{array} \right.$ 136. |
| Methylhexyl carbinol | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{C}(\text{C}_4\text{H}_9)\text{HH}_o \end{array} \right.$ 184. |
| Methylnonyl carbinol | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{C}(\text{C}_6\text{H}_{13})\text{HH}_o \end{array} \right.$ 229. |

The first is obtained by the action of nascent hydrogen on acetone:—



The relation existing between ethylic alcohol, propylic alcohol, and isopropylic alcohol, will at once be evident from the following formulæ:—



From these formulæ it is seen that propylic alcohol is ethylic alcohol in which one atom of hydrogen in the methyl (or *non-oxygenated* part of the compound) is displaced by methyl; whereas isopropylic alcohol is ethylic alcohol in which one atom of hydrogen in the *oxygenated* part of the compound is displaced by methyl.

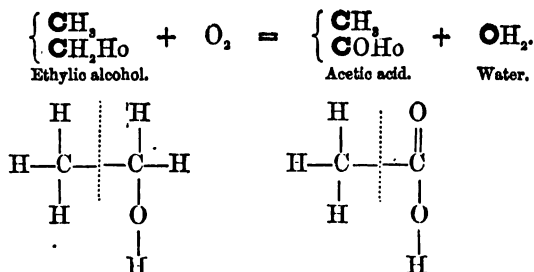
Ethylic alcohol boils at ... 78°·4

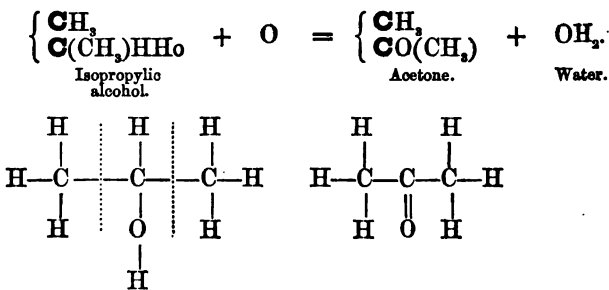
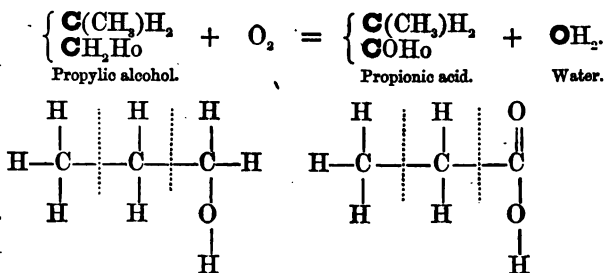
Propylic alcohol „ ... 97

Isopropylic alcohol „ ... 84

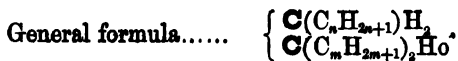
Thus, by substituting an atom of methyl for one of hydrogen in the non-oxygenated part of the alcohol, the addition of CH_3 raises the boiling-point 18°·6; whilst, if an atom of hydrogen in the oxygenated part be similarly displaced, the same addition only raises the boiling-point 5°·6.

Isopropylic alcohol yields by oxidation a ketone, and not an acid. The radical oxatyl being a necessary constituent in organic acids, it will be seen from the following equations that, although propylic alcohol can be converted into an acid without the disruption of its carbon atoms, isopropylic alcohol cannot be so transformed:—





TERTIARY MONOHYDRIC ALCOHOLS.

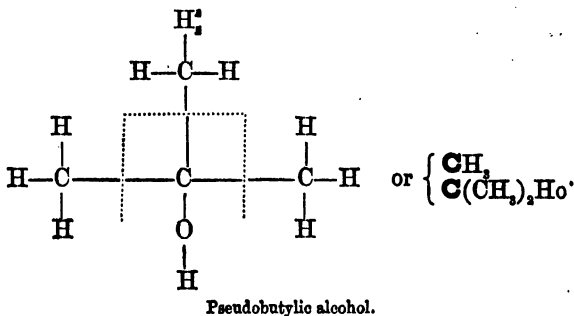
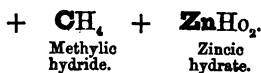
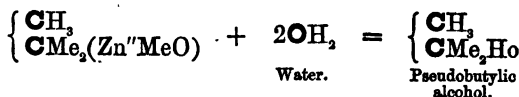
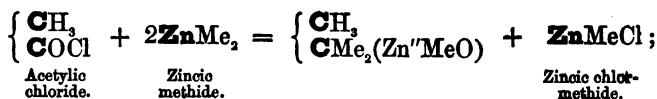


The following members of this series are known :—

| | | Boiling- points. |
|--|---|---------------------|
| Pseudobutylic alcohol or } trimethyl carbinol | CMe_3Ho | 82°.5. |
| Dimethylethyl carbinol ... | CEtMe_2Ho | 100°. |
| Dimethylpropyl carbinol | CPrMe_2Ho | 120°. |
| Dimethylisopropyl carbinol | $\text{C}\beta\text{PrMe}_2\text{Ho}$ | 112°. |
| Methyldiethyl carbinol ... | CEt_2MeHo | 115°. |
| Triethyl carbinol | CEt_3Ho | 141°. |
| Diethylpropyl carbinol ... | CPrEt_2Ho | — |

Pseudobutylic alcohol, $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CMe}_2\text{Ho} \end{array} \right.$, exists in small quantities

in butylic alcohol obtained by fermentation; it has also been produced by acting with zinc methide on acetylic chloride, and submitting the product thus obtained to the action of water:—



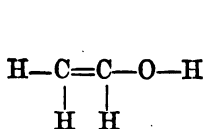
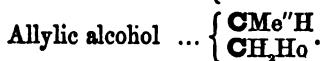
CHAPTER VII.

MONOHYDRIC ALCOHOLS:

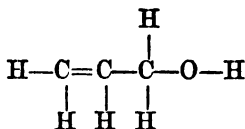
Vinyl or $\text{C}_n\text{H}_{2n-1}\text{Ho}$ series.

Two alcohols only of this series are known; of these the first

is a secondary, and the second a normal alcohol :



Vinyl alcohol.

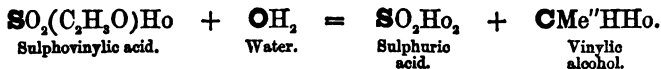
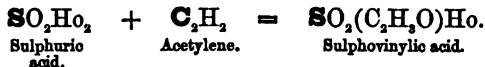


Allylic alcohol.

VINYLIC ALCOHOL.



Preparation.—By combining acetylene with sulphuric acid and distilling the product with water, in the same manner as in the preparation of ethylic alcohol from ethylene (p. 54) :—

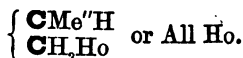


This alcohol is isomeric with aldehyde and with ethylenic oxide :—



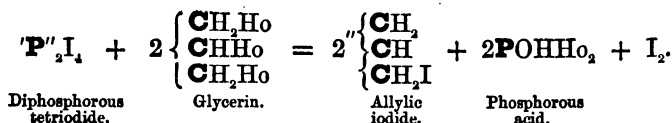
If the above, and not $\left\{ \begin{array}{l} \text{CH} \\ \text{CH}_2\text{Ho} \end{array} \right.$ be the true formula for vinyl alcohol from acetylene, it is obvious that this body could not yield an acid by oxidation ; but if the latter formula represents it, this alcohol is normal and ought to yield on oxidation an acid, $\left\{ \begin{array}{l} \text{CH} \\ \text{COHo} \end{array} \right.$ homologous with acrylic acid.

ALLYLIC ALCOHOL.

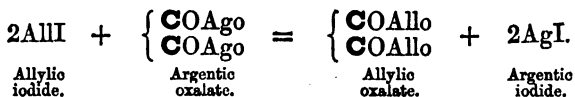


Boils at 96°·5. Sp. gr. of liquid at 0° = 0·8709.

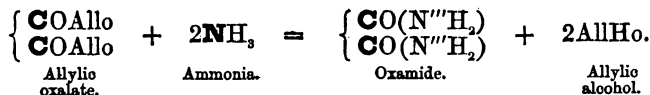
Preparation.—Glycerin, when submitted to the action of di-phosphorus tetriodide, yields allylic iodide:—



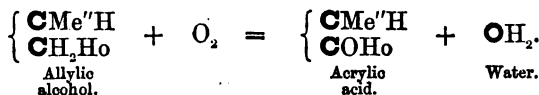
The allylic iodide is then decomposed by argentic oxalate, when allylic oxalate is formed:—



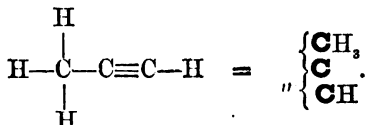
The allylic oxalate is next decomposed by ammonia, when oxamide and allylic alcohol are produced:—



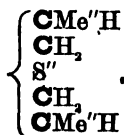
Reactions.—1. In all ordinary reactions, allylic alcohol behaves like ethylic alcohol. By oxidation it gives acrylic acid:—



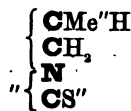
2. With phosphoric anhydride it yields allylene:—



Among the ethereal salts of allylic alcohol, the sulphide and sulphocyanate occur in nature as garlic and mustard oils :—



Allylic
sulphide.
(Garlic oil.)



Allylic
sulphocyanate.
(Mustard oil.)

CHAPTER VIII.

MONOHYDRIC ALCOHOLS:

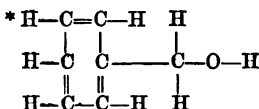
Phenyl or $\text{C}_n\text{H}_{2n-7}$ series.

These alcohols may be divided into a normal and a tertiary class. The members of the first class possess the general character of the normal alcohols of the ethyl series, while those of the second class exhibit a slightly acid character.

CLASS I. Normal Alcohols.

General formula..... $\left\{ \begin{array}{l} \text{C}_n\text{H}_{2n-7} \\ \text{CH}_2\text{HO} \end{array} \right.$

Benzylic alcohol* $\left\{ \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{CH}_2\text{HO} \end{array} \right.$



| | |
|---------------------------|---|
| Xylylic alcohol | $\left\{ \begin{array}{l} \text{C}_6\text{MeH}_4 \\ \text{CH}_2\text{Ho} \end{array} \right.$ |
| Cumylic alcohol | $\left\{ \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{CH}_2\text{Ho} \end{array} \right.$ |
| Sycocerylic alcohol | $\left\{ \begin{array}{l} \text{C}_{17}\text{H}_{37} \\ \text{CH}_2\text{Ho} \end{array} \right.$ |

CLASS II. Tertiary Alcohols.

| | |
|---|--|
| General formula..... | $\text{C}_n\text{H}_{2n-7}\text{Ho}.$ |
| Phenylic alcohol. Carbo- lic acid* | $\text{C}_6\text{H}_5\text{Ho}.$ |
| Cresylic alcohol | $\text{C}_6\text{MeH}_4\text{Ho}.$ |
| Phlorol..... | $\text{C}_6\text{EtH}_4\text{Ho}.$ |
| Dimethyl-phenylic alcohol | $\text{C}_6\text{Me}_2\text{H}_3\text{Ho}.$ |
| Thymylic alcohol..... | $\text{C}_6\text{Et}_2\text{H}_3\text{Ho} ?$ |

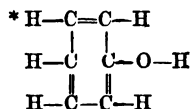
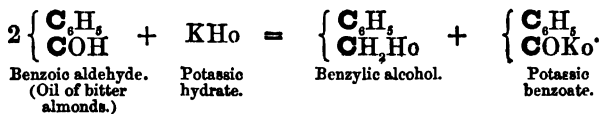
CLASS I. NORMAL ALCOHOLS.

BENZYLIC ALCOHOL.

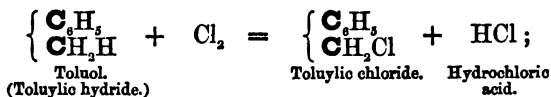


Boils at 204°.

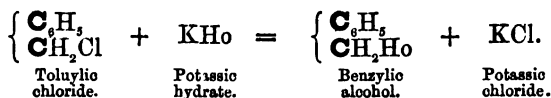
Preparation.—1. By treating oil of bitter almonds with alcoholic potash :—



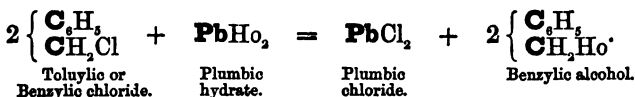
2. Benzylic alcohol may be obtained from toluol by first converting the latter into toluylic chloride by the action of chlorine—



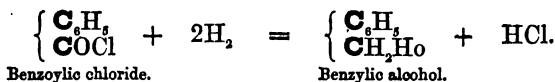
and then submitting the toluylic chloride to the action of potassic hydrate :—



3. By digesting benzylic chloride with freshly precipitated plumbic hydrate :—

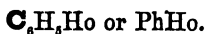


4. By passing a mixture of hydrogen and the vapour of benzoyle chloride over heated spongy palladium :—



CLASS II. TERTIARY ALCOHOLS.

PHENYLIC ALCOHOL, *Carbolic Acid, Phenylic Acid.*



Molecular weight = 94. *Molecular volume* $\square\square$. 1 litre of phenylic alcohol vapour weighs 47 criths. *Sp. gr.* 1.065 at 18°. *Fuses at* 34°. *Boils at* 188°.

Occurrence.—In coal-tar, and in small quantity in the urine of man, of the cow, and of the horse.

Preparation.—1. By the distillation of salicylic acid with baryta or lime :—



2. It is also produced in the destructive distillation of numerous organic substances.

3. Phenyllic alcohol is formed when the vapour of ethylic alcohol or acetic acid is passed through a red-hot tube. In this manner phenylic compounds may be obtained from their elements ; for both acetic acid and alcohol may be built up from carbon, hydrogen, and oxygen.

4. Phenyllic alcohol is generated when aniline hydrochlorate is treated with potassic nitrite :—



Reactions.—Treated with chlorine, bromine, or nitric acid, phenylic alcohol produces a series of substitution products, of which the following are examples :—

| | |
|--|--|
| Dichlorphenylic acid..... | $\text{C}_6\text{H}_3\text{Cl}_2\text{Ho}.$ |
| Trichlorphenylic acid..... | $\text{C}_6\text{H}_2\text{Cl}_3\text{Ho}.$ |
| Perchlorphenylic acid | $\text{C}_6\text{Cl}_6\text{Ho}.$ |
| Bromphenylic acid..... | $\text{C}_6\text{H}_4\text{BrHo}.$ |
| Nitrophenylic acid..... | $\text{C}_6\text{H}_4(\text{N}^{\circ}\text{O}_2)\text{Ho}.$ |
| Dinitrophenylic acid..... | $\text{C}_6\text{H}_3(\text{N}^{\circ}\text{O}_2)_2\text{Ho}.$ |
| Trinitrophenylic acid. (<i>Picric acid.</i>) | $\text{C}_6\text{H}_2(\text{N}^{\circ}\text{O}_2)_3\text{Ho}.$ |
| Amidodinitrophenylic acid. | |
| (<i>Picramic acid.</i>)..... | $\text{C}_6\text{H}_2(\text{N}^{\circ}\text{H}_2)(\text{N}^{\circ}\text{O}_2)_2\text{Ho}.$ |

CRESYLIC ALCOHOL.



Boils at 204°.

This alcohol is contained in creosote; it is isomeric with benzylic alcohol.

CHAPTER IX.

DIHYDRIC ALCOHOLS.

Glycol or $\text{C}_n\text{H}_{2n}\text{Ho}_2$ series.

The following is a list of the glycols at present known, with their probable constitutional formulæ:—

| | | | Boiling-points. |
|--------------------------------|--|--|-----------------|
| Glycol or Ethylic glycol | $\text{C}_2\text{H}_6\text{O}_2$ or | $\begin{Bmatrix} \text{CH}_2\text{Ho} \\ \text{CH}_2\text{Ho} \end{Bmatrix}$ | 197°5. |
| Propylic glycol... | $\text{C}_3\text{H}_8\text{O}_2$ or | $\begin{Bmatrix} \text{CMeHHo} \\ \text{CH}_2\text{Ho} \end{Bmatrix}$ | 188°–189°. |
| Butylic glycol ... | $\text{C}_4\text{H}_{10}\text{O}_2$ or | $\begin{Bmatrix} \text{CEtHHo} \\ \text{CH}_2\text{Ho} \end{Bmatrix}$ | 183°–184°. |
| Amylic glycol ... | $\text{C}_5\text{H}_{12}\text{O}_2$ or | $\begin{Bmatrix} \text{CPrHHo} \\ \text{CH}_2\text{Ho} \end{Bmatrix}$ | 177°. |

Methylic glycol has not been obtained.

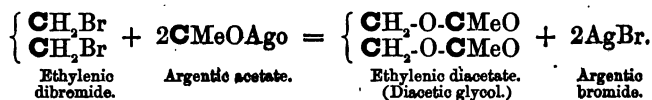
The existence of normal, secondary, &c. alcohols of this subdivision has not yet been clearly established; but ethylic glycol is probably a normal glycol, whilst propylic, butylic, and amylic glycols are generally considered to be secondary glycols, as shown in the above formulæ.

It will be observed that the boiling-points of the glycols differ from each other in a direction inversely to that previously noticed in the case of the normal monohydric alcohols: the more complex substances boil at a lower temperature than the simpler ones.

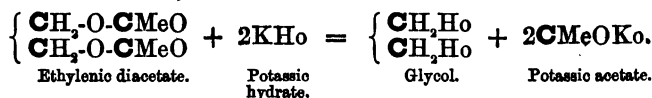
GLYCOL. ETHYLIC GLYCOL, *Ethylenic Alcohol.*

Molecular weight = 62. *Molecular volume* $\square\square$. 1 litre of ethylic glycol vapour weighs 31 criths. *Sp. gr.* 1.125. Boils at 197°.5.

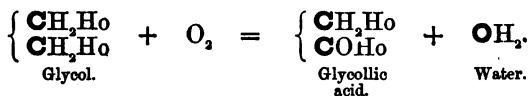
Preparation.—Ethylenic dibromide is treated with argentic acetate, and thus converted into ethylenic diacetate:—



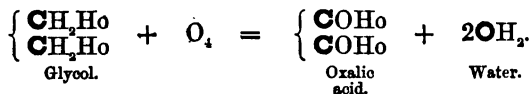
The ethylenic diacetate is now acted upon by potassic hydrate, and yields potassic acetate and glycol:—



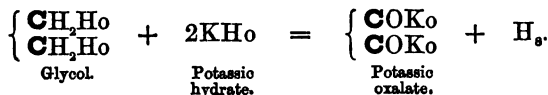
Reactions.—1. Glycol is easily oxidized, the first product of its oxidation being glycollic acid:—



2. By further oxidation oxalic acid is formed:—



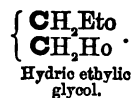
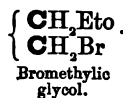
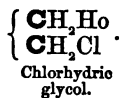
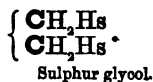
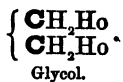
3. Potassic oxalate is produced by heating glycol and potassic hydrate together to 250°:—



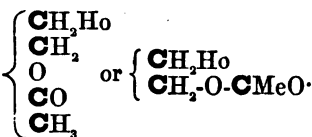
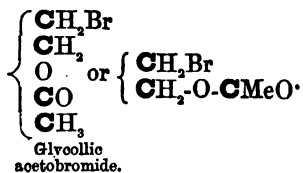
4. Treated with potassium or sodium, the hydrogen of the hydroxyl in glycol is replaced in two successive stages :—



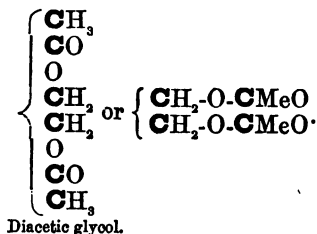
The following list contains some of the principal derivatives of glycol :—

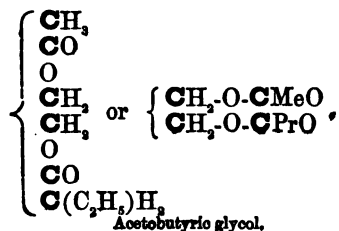


Diethylic glycol.



Monacetic glycol.

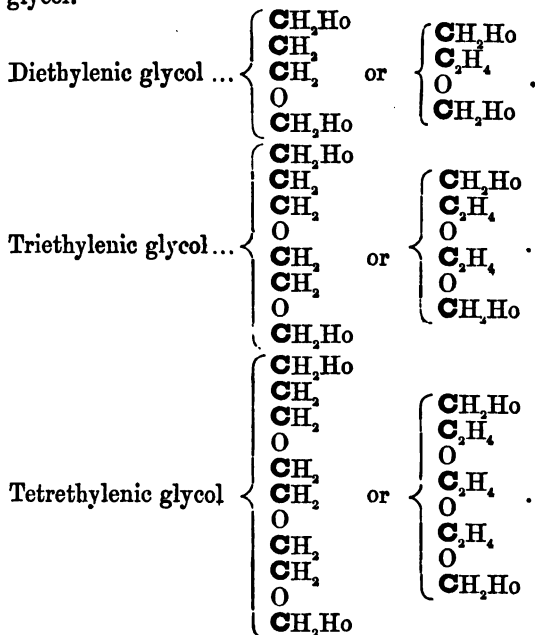




POLYETHYLENIC GLYCOLS,

Polyethylenic Alcohols.

These bodies are produced by heating ethylenic oxide with glycol in sealed tubes, and by other processes. They may be regarded as formed by the addition of ethylenic oxide to glycol.



Pentethylenic and hexethylenic glycols have also been formed.

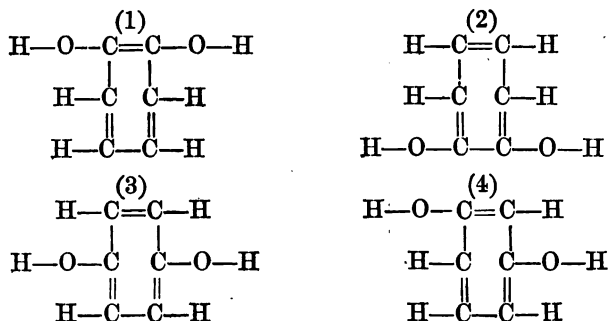
CHAPTER X.

*DIHYDRIC ALCOHOLS.*Orcin or $C_nH_{2n-8}Ho_2$ series.

Like the phenyl series, the orcin series of alcohols are the derivatives of benzol. The following alcohols belonging to this series have been described :—

| | | Melting-point. |
|---------------------------|------------------------|----------------|
| Hydroquinone | } $C_6H_4Ho_2$ | 177°·5 |
| Resorcin | | 99°·0 |
| Pyrocatechin or Oxyphenol | | 111°·5 |
| Orcin | } $C_6MeH_3Ho_2$ | 86°·0 |
| Homopyrocatechin | | — |
| Betaorcin | | — |
| | $C_6Me_2H_2Ho_2$ | — |

Theory indicates the existence of four isomeric bodies of the formula $C_6H_4Ho_2$, the graphic formulæ of which are thus written :—



The isomerism of 1, 3, and 4, and of 2, 3, and 4 is caused (symbolically speaking) by the different distances from each other of the two atoms of carbon with which the two semi-molecules of hydroxyl are combined; in 1 and 2 these carbon atoms are neighbours, in 4 they are separated by one inter-

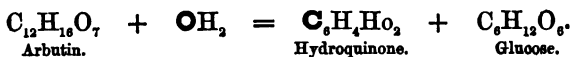
vening atom of carbon, and in 3 by two intervening atoms of carbon. The isomerism of Nos. 1 and 2 is not equally obvious; indeed it has been overlooked by Kekulé, who considers that three modifications only of the formula $C_6H_4HO_2$ are possible, unless the six atoms of hydrogen in benzol be not regarded as of equal value. An inspection of the above graphic formulæ shows, however, that a fourth modification is possible, dependent upon the mode in which the two neighbouring atoms of hydroxylic carbon are joined together. In No. 1 these atoms are united by two bonds, in No. 2 by only one bond.

It is at present impossible to assign to each of the three known isomers of $C_6H_4HO_2$ its own constitutional formula. The same is the case also with the remaining alcohols of this series.

HYDROQUINONE.



Preparation.—1. By treating arbutin with emulsin, or by boiling it with dilute sulphuric acid:—



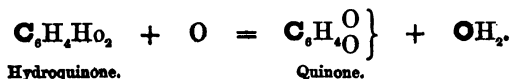
2. By the action of sulphurous acid upon a solution of quinone.

3. By the destructive distillation of quinic acid.

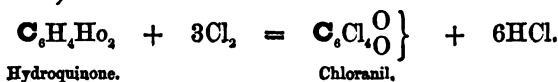
Reactions.—1. Passed in vapour through a red-hot tube, it is decomposed into quinone and hydrogen:—



2. By many oxidizing agents it is transformed into quinone:—



3. By the action of chlorine or a mixture of potassic chlorate and hydrochloric acid, it is converted into perchloro-quinone (chloranil):—



ORCIN.



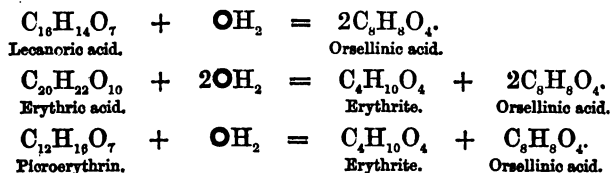
Melts at 86°. Boils at about 290°.

Occurrence.—In certain lichens, such as *Lecanora tartarea*, *Roccella tinctoria*, and *Variolaria orcina*.

Preparation.—By the dry distillation of orsellinic acid, or by boiling this acid with powerful bases:—



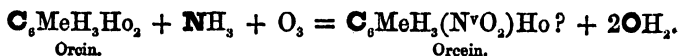
Many other bodies which are obtained from lichens, such as lecanoric acid, erythrin, and picroerythrin, yield orcin under similar treatment; but all these compounds give first orsellinic acid, which then breaks up into orcin and carbonic anhydride; thus:—



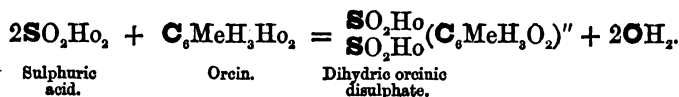
Reactions.—1. With chlorine, bromine, iodine, and nitric acid, orcin gives the following substitution products:—

| | | Melting-point. |
|---------------------------|--|----------------|
| Monobromorcin | $\text{C}_6\text{MeH}_2\text{BrH}_2\text{O}_2$ | 135° |
| Tribromorcin | $\text{C}_6\text{MeBr}_3\text{H}_2\text{O}_2$ | 103° |
| Trichlororcin | $\text{C}_6\text{MeCl}_3\text{H}_2\text{O}_2$ | 159° |
| Triiodorcin | $\text{C}_6\text{MeI}_3\text{H}_2\text{O}_2$ | — |
| Trinitro-orcinic acid ... | $\text{C}_6\text{Me}(\text{NO}_2)_3\text{H}_2\text{O}_2$ | 162° |

2. By treatment with ammonia in the presence of free oxygen it yields orcein, the colouring-matter of *Archil* and *Cudbear*, the reaction being probably the following :—



3. Heated with an excess of concentrated sulphuric acid to a temperature of from 60° to 80°, orcin yields orcin-disulphuric acid (dihydric orcinic disulphate) :—



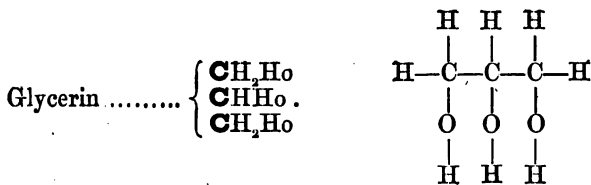
CHAPTER XI.

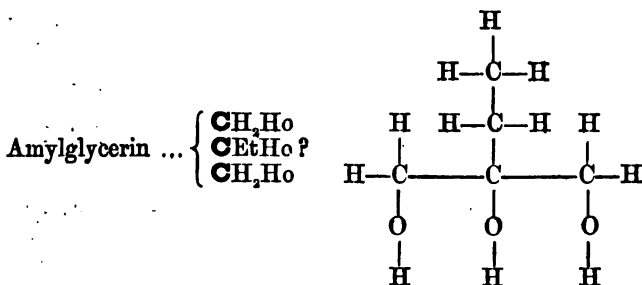
TRIHYDRIC ALCOHOLS.

Glycerin or $\text{C}_n\text{H}_{2n-1}\text{Ho}_3$ series.

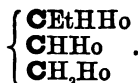
These alcohols contain three semimolecules of hydroxyl united with three different atoms of carbon; consequently the lowest term of the series contains three atoms of carbon.

Only two of these alcohols have been hitherto obtained :—



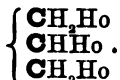


The constitution of amylglycerin is not at present established. Its formula may possibly be



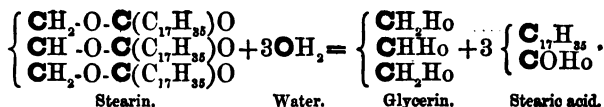
The action of oxidizing agents on amylglycerin will probably throw light upon its internal structure.

GLYCERIN.



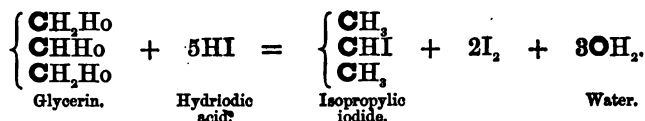
Sp. gr. of liquid at 15°4 is 1.26. Crystallizes at low temperatures, and remains solid afterwards at ordinary temperatures. Boils in vacuo at 179°5.

Sources.—Most animal and vegetable fats consist of mixtures of the glycerin ethereal salts of the fatty, and of the oleic, series of acids. Glycerin is liberated from these by water at high temperatures, or by bases giving salts insoluble in water:—

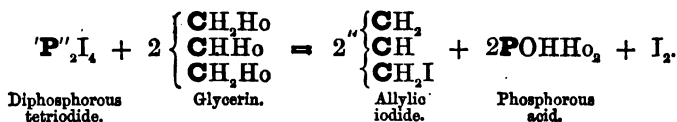


Relation of Glycerin to Isopropylic Alcohol.

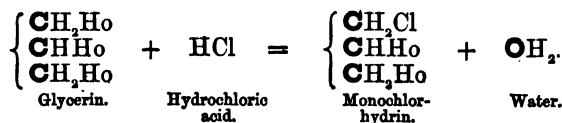
By the action of hydriodic acid, glycerin is converted into isopropylic iodide:—

*Relation of Glycerin to Allylic Alcohol.*

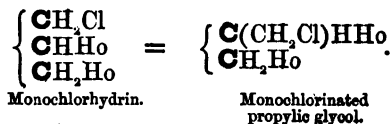
When diphosphorous tetriodide is brought into contact with glycerin, an energetic reaction ensues, allylic iodide being formed:—

*Relations of Glycerin to Propylic Glycol.*

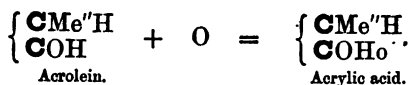
The several semimolecules of hydroxyl in glycerin are capable of being replaced by chlorine, bromine, &c.; thus, by the action of hydrochloric acid on glycerin, one semimolecule of hydroxyl is displaced by chlorine, monochlorhydrin being formed:—



Monochlorhydrin is identical with monochlorinated propylic glycol:—



By the absorption of oxygen, acrolein is transformed into acrylic acid:—



Both these reactions are accomplished simultaneously when glycerin is added to fused potassic hydrate:—



CHAPTER XII.

TRIHYDRIC ALCOHOLS.

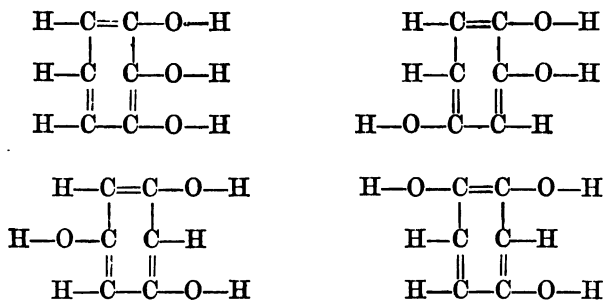
Pyrogallic or $\text{C}_n\text{H}_{2n-3}\text{Ho}_3$ series.

Like the phenyl and orcin series, these alcohols are the direct derivatives of benzol.

The following bodies are believed to belong to this series, whilst several other compounds not yet sufficiently known will probably soon be added to it:—

| | | Melting-point. |
|-----------------------|--|---|
| Pyrogallin | $\left. \begin{array}{l} \text{Pyrogallin} \dots\dots\dots \\ \text{Phloroglucin} \dots\dots\dots \\ \text{Phenomalic acid ?} \dots \end{array} \right\} \text{C}_6\text{H}_3\text{Ho}_3 \dots\dots$ | $\left\{ \begin{array}{l} 115^\circ. \\ 220^\circ. \\ \text{—} \end{array} \right.$ |
| Phloroglucin | | |
| Phenomalic acid ? ... | | |

Theory points to four isomeric modifications of the formula $\text{C}_6\text{H}_3\text{Ho}_3$, viz. :—



It is at present impossible to assign any of these formulæ to the above enumerated three members of this series of alcohols.

PYROGALLIN, *Pyrogallic Acid*.



Melts at 115°. Sublimes with partial decomposition at 210°.

Preparation.—1. By heating gallic acid to 210°–220° in a stream of carbonic anhydride :—



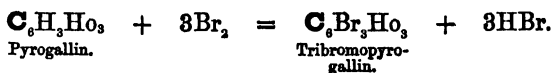
2. By heating gallic acid with twice or thrice its weight of water to 200°–210° for half an hour in a Papin's digester. The reaction is the same as in No. 1.

Reactions.—1. Does not neutralize alkalies or form true salts.

2. Passed over heated zinc, it is transformed into benzol :—



3. Bromine converts pyrogallin into tribromopyrogallin:—



4. Heated to 250° , it yields water and metagallic acid:—



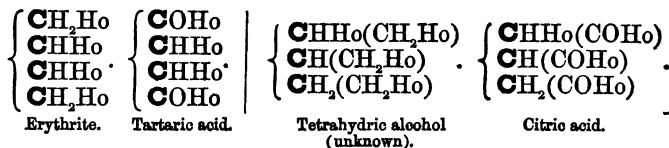
5. Ammonia in the presence of air forms with it pyrogallein, to which the formula $\text{C}_{18}\text{H}_{20}\text{N}_6\text{O}_{10}$ has been assigned.

6. Concentrated boiling solution of caustic potash decomposes it into acetic, oxalic, and carbonic acids.

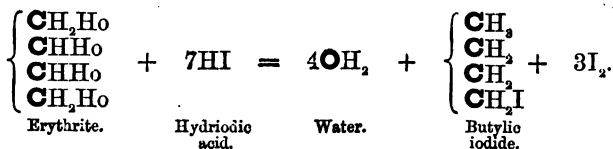
7. An alkaline solution of pyrogallin rapidly absorbs free oxygen, forming a dark-coloured body, together with acetic and carbonic acids and a small quantity of carbonic oxide.

OTHER POLYHYDRIC ALCOHOLS.

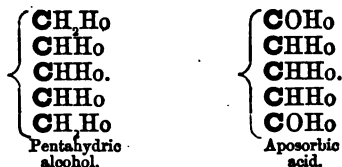
Erythrite (*Erythroglucin*, *Erythromannite*, *Phycite*, *Pseudorcin*) is a tetrahydric alcohol; and the acid corresponding to it is tartaric acid. Citric acid may also be considered as derived from an unknown alcohol of this series. A glance at the formulæ of these alcohols and acids will show their relations:—



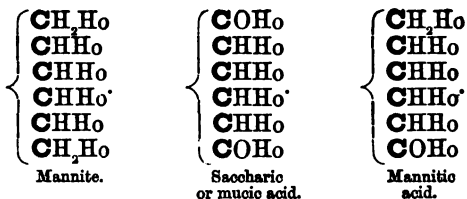
When reduced by hydriodic acid, erythrite yields butylic iodide:—



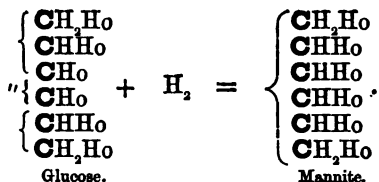
Pinite and *Quercite* are believed to be pentahydric alcohols; and *aposorbic acid* is probably a derivative of one of them:—



Mannite is a hexahydric alcohol. There are three acids corresponding to this alcohol: these are *saccharic* and *mucic acids*, which are isomeric, and *mannitic acid*:—



Mannite is closely related to *glucose*, the latter containing two atoms of hydrogen less than the former. *Glucose* can, in fact, be converted into *mannite* by the action of nascent hydrogen:—



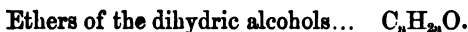
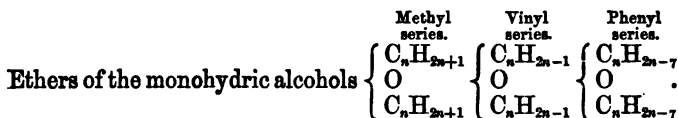
Alcohols of high hydricity possess a sweet taste, in fact with increase of hydricity the alcohols gradually pass into saccharine substances or sugars.

CHAPTER XIII.

THE ETHERS.

THESE compounds are the oxides of the positive radicals.

Each series of alcohols produces a series of ethers; we have thus ethers of the monohydric, dihydric, and trihydric alcohols, of which the following are the general formulæ :—

*ETHERS OF THE MONOHYDRIC ALCOHOLS.*

These bodies are derived from the alcohols by the substitution of the hydroxylic hydrogen contained in the latter by a positive monad radical.

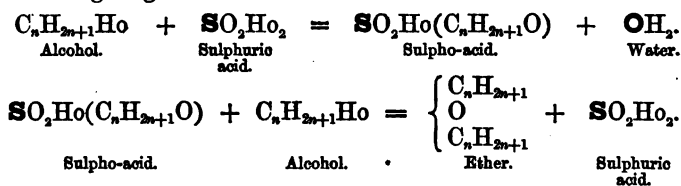
METHYL SERIES.

The following list contains some of the ethers of this series :—

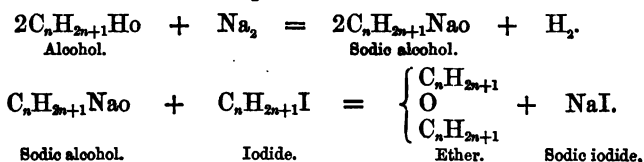
| | | | | Boiling- points. |
|----------------------|--|----|--|-------------------------|
| Methylic ether | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{CH}_3 \end{array} \right\}$ | or | OMe_2 | -21°. |
| Methylicethylicether | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{C}_2\text{H}_5 \end{array} \right\}$ | or | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{CMeH}_2 \end{array} \right\}$ | or OMeEt +11°. |
| Ethylic ether | $\left\{ \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{O} \\ \text{C}_2\text{H}_5 \end{array} \right\}$ | or | $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{O} \\ \text{CMeH}_2 \end{array} \right\}$ | or OEt_2 35°6. |
| Methylicamylicether | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{C}_5\text{H}_{11} \end{array} \right\}$ | or | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{CBuH}_2 \end{array} \right\}$ | or OMeAy 92°. |

| | | | | | Boiling points. |
|------------------------|--|----|--|-------------------|--------------------|
| Ethylie butylic ether. | $\begin{cases} \text{C}_2\text{H}_5 \\ \text{O} \\ \text{C}_4\text{H}_9 \end{cases}$ | or | $\begin{cases} \text{CMeH}_2 \\ \text{O} \\ \text{CPrH}_2 \end{cases}$ | or OEtBu | 80°? |
| Ethylie amylic ether. | $\begin{cases} \text{C}_2\text{H}_5 \\ \text{O} \\ \text{C}_5\text{H}_{11} \end{cases}$ | or | $\begin{cases} \text{CMeH}_2 \\ \text{O} \\ \text{CBuH}_2 \end{cases}$ | or OEtAy | 112°. |
| Butylic ether | $\begin{cases} \text{C}_4\text{H}_9 \\ \text{O} \\ \text{C}_4\text{H}_9 \end{cases}$ | or | $\begin{cases} \text{CPrH}_2 \\ \text{O} \\ \text{CPrH}_2 \end{cases}$ | or OBu_2 | 104°. |
| Amylic ether | $\begin{cases} \text{C}_5\text{H}_{11} \\ \text{O} \\ \text{C}_5\text{H}_{11} \end{cases}$ | or | $\begin{cases} \text{CBuH}_2 \\ \text{O} \\ \text{CBuH}_2 \end{cases}$ | or OAy_2 | 176°. |

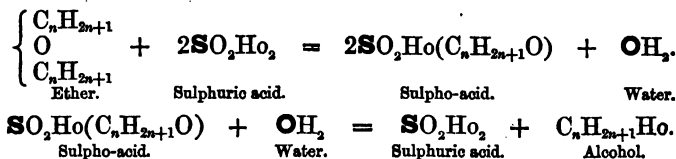
Formation.—1. By the action of sulphuric acid upon the $\text{C}_n\text{H}_{2n+1}\text{Ho}$ alcohols. The process may be divided into the two following stages:—

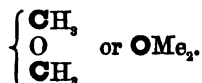


2. By converting the $\text{C}_n\text{H}_{2n+1}\text{Ho}$ alcohols into sodium or potassium compounds, and then acting upon the latter with the iodides of the monad positive radicals:—



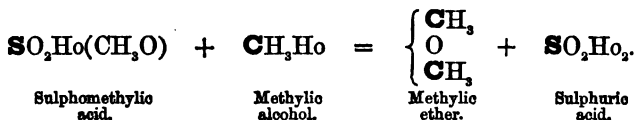
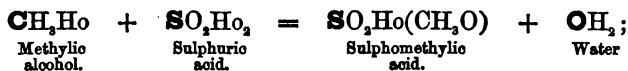
Reaction.—The ethers can be reconverted into the corresponding alcohols by treating them with sulphuric acid, and then distilling, with water, the sulpho-acid so produced:—



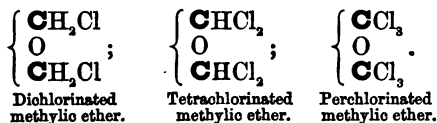
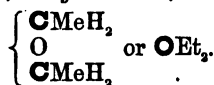
METHYLIC ETHER, *Methylic Oxide.*

Molecular weight = 46. *Molecular volume* $\square\square$. 1 litre of *methylic ether vapour weighs 23 criths.* *Boils at* -21° .

Preparation.—By heating methylic alcohol with sulphuric acid or boric anhydride:—



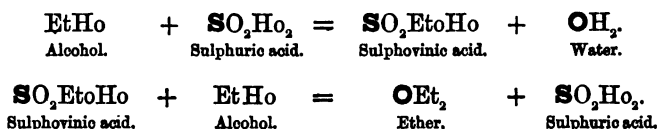
Reaction.—Methylic ether is acted upon by chlorine under the influence of light, the hydrogen being displaced atom for atom by chlorine. The following compounds are formed:—

**ETHYLIC ETHER, *Ethylic Oxide, Ether, Sulphuric Ether.***

Molecular weight = 74. *Molecular volume* $\square\square$. 1 litre of *ether vapour weighs 37 criths.* *Sp. gr.* = 0.723. *Fuses at* -31° . *Boils at* $35^\circ.6$.

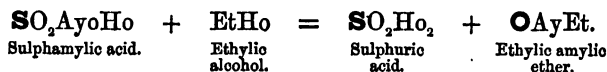
Preparation.—A mixture of equal volumes of sulphuric acid and alcohol is heated to a temperature of from 140° to 145° , and

a constant stream of alcohol is allowed to flow into the mixture. Ether and water distil over together. Two reactions take place successively : in the first, the alcohol is converted into sulphovinic acid ; and in the second the sulphovinic acid is converted by a further quantity of alcohol into sulphuric acid and ether :—



In this manner the same quantity of sulphuric acid can convert an unlimited quantity of alcohol into ether.

The formation of ether is not due to the simple removal of water from two molecules of alcohol by sulphuric acid. This is proved, first, by the sulphuric acid not becoming more dilute, and, secondly, by the fact that, if sulphamylic acid be acted upon by ethylic alcohol, the mixed ethylic amylic ether is formed:—

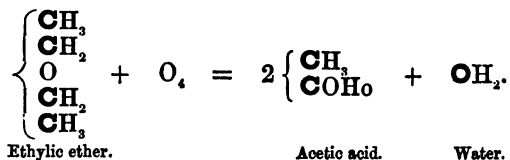


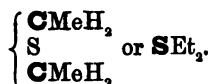
Reactions.—1. Ethylic ether, when mixed with an equal volume of sulphuric acid, produces sulphovinic acid:—



2. Hot nitric acid converts ethylic ether into carbonic, acetic, and oxalic acids.

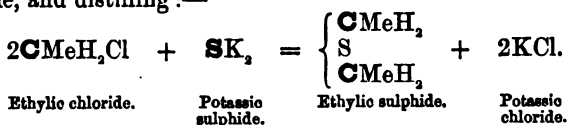
3. Exposed to the air, it gradually absorbs oxygen and is transformed into acetic acid:—



ETHYLIC SULPHIDE, *Sulphur Ether.*

Molecular weight = 90. *Molecular volume* $\square\square$. 1 litre of ethylic sulphide vapour weighs 45 criths. Boils at 73°.

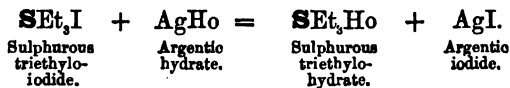
Preparation.—By adding ethylic chloride to potassic sulphide, and distilling:—



Reactions.—1. Ethylic sulphide combines directly with ethylic iodide, forming



By the action of argentic oxide on this iodide, the corresponding hydrate may be formed:—



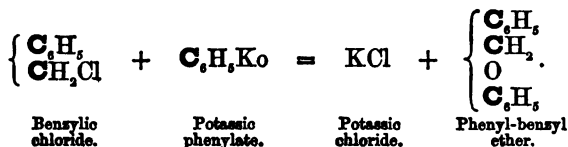
2. By cold nitric acid it is converted into sulphurous diethoxide (SOEt_2), which by more powerful oxidizing agents is transformed into diethylsulphon (sulphuric diethoxide), SO_2Et_2 , which melts at 70° and boils at 248°.

ETHERS OF THE VINYL AND PHENYL SERIES.

Of the ethers of the vinyl series, allylic ether, $\begin{Bmatrix} \text{C}_3\text{H}_5 \\ \text{O} \\ \text{C}_3\text{H}_5 \end{Bmatrix}$, alone is known. It boils at 82°.

In the phenyl series, phenylic ether, $\begin{Bmatrix} \text{C}_6\text{H}_5 \\ \text{O} \\ \text{C}_6\text{H}_5 \end{Bmatrix}$, and benzylic ether, $\begin{Bmatrix} \text{C}_7\text{H}_7 \\ \text{O} \\ \text{C}_7\text{H}_7 \end{Bmatrix}$, have been obtained.

By digesting benzylic chloride with potassic phenylate, a mixed ether, phenyl-benzyl ether, is formed:—

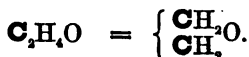


ETHERS OF THE DIHYDRIC ALCOHOLS.

Of these the three following are known, but the first only has been carefully studied:—

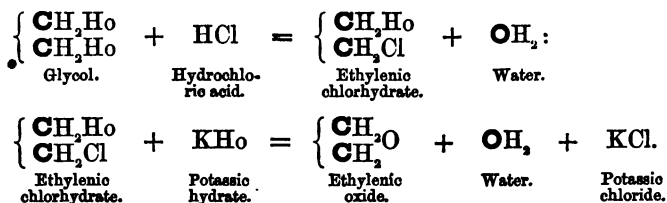
| | Boiling-points. |
|---|-----------------|
| Ethylenic oxide, $\text{C}_2\text{H}_4\text{O}$ | 13°·5. |
| Propylenic oxide, $\text{C}_3\text{H}_6\text{O}$ | 35°·0. |
| Amylenic oxide, $\text{C}_5\text{H}_{10}\text{O}$ | 95°·0. |

ETHYLENIC OXIDE, *Ethylenic Ether*.

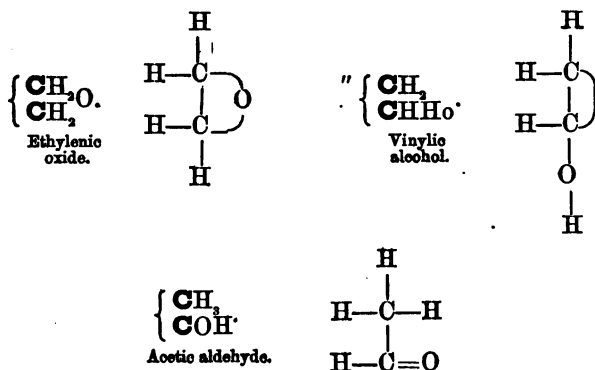


Molecular weight = 44. *Molecular volume* $\square\square$. 1 litre of *ethylenic oxide vapour weighs 22 criths*. *Boils at 13°·5*.

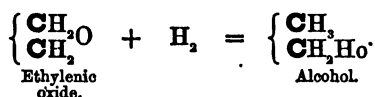
Preparation.—Ethylenic oxide is obtained from glycol by converting the latter, first into ethylenic chlorhydrate, or chlorhydric glycol, by the action of hydrochloric acid, and subsequently treating the compound thus formed with potassic hydrate:—



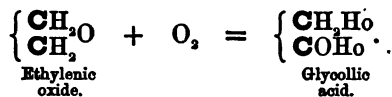
Isomers.—Ethylenic oxide is isomeric with vinylic alcohol and acetic aldehyde. The nature of this isomerism is seen in the following formulæ:—



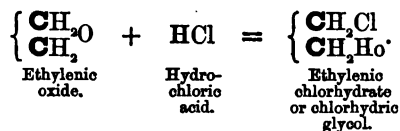
Reactions.—1. Ethylenic oxide unites with nascent hydrogen, forming alcohol:—



2. It also unites with oxygen, forming glycollic acid:—

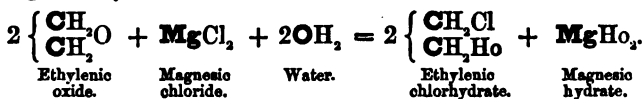


3. It is a basic substance, and unites directly with acids:—

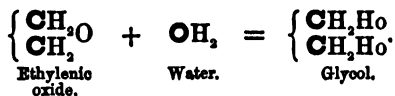


4. Ethylenic oxide precipitates as hydrates many metals from

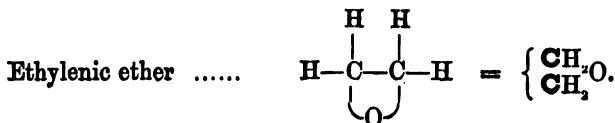
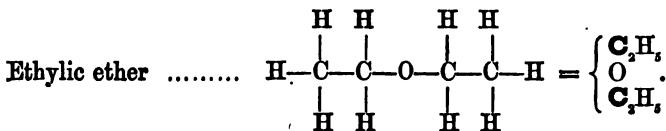
solutions of their salts, such as the ferric, aluminic, cupric, and magnesian hydrates :—



5. It also combines directly with water, reproducing glycol :—



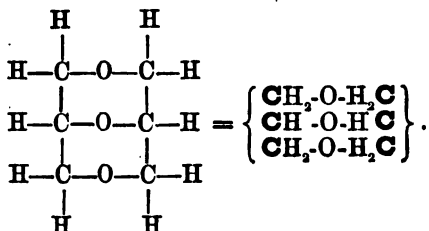
These reactions exhibit a wide difference between the behaviour of ethylenic ether and that of ethylic ether. This difference arises from the fact, that in ethylic ether the ethyl semimolecules are held together by the oxygen only, whereas in ethylenic ether the linking of the two groups of CH_2 does not depend on the oxygen atom alone, as will be seen from the following formulæ :—



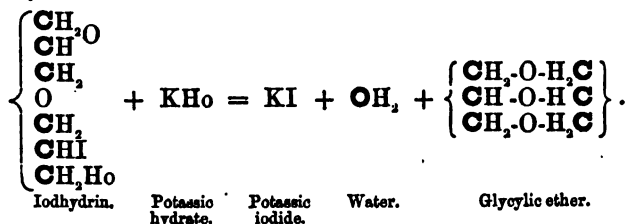
On account of this peculiarity of constitution, ethylenic oxide can combine directly with many substances without the disruption of its molecule,—a property which obviously cannot be possessed by ethylic ether.

ETHERS OF THE TRIHYDRIC ALCOHOLS.

Of these only one is known, viz. :—

GLYCYLIC ETHER, *Glycylic Oxide.*

Preparation.—By the action of potassic hydrate on so-called iodhydrin:—

**CHAPTER XIV.****THE HALOID ETHERS.**

EACH series of positive radicals forms its own series of haloid ethers.

These ethers are produced by the substitution of hydroxyl in the alcohols by chlorine, bromine, iodine, fluorine, or cyanogen.

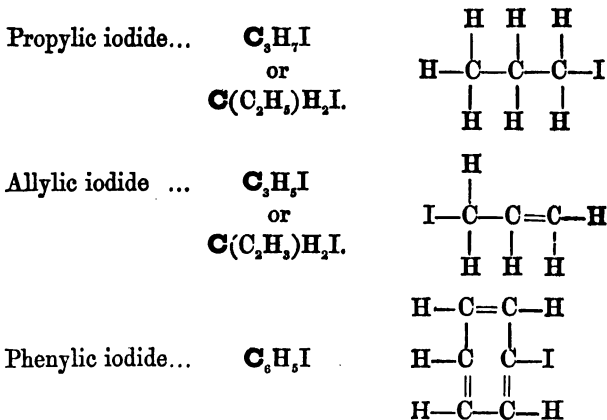
Haloid Ethers of the Monad Positive Radicals.

As these radicals can only unite with one semimolecule of

hydroxyl, they can only form one haloid ether. Each series of radicals therefore forms one series of haloid ethers:—

- I. Haloid ethers of the form $C_nH_{2n+1}Cl$.
 II. " " " " " $C_nH_{2n-1}Cl$.
 III. " " " " " $C_nH_{2n-7}Cl$.

The following will serve as examples of the three series:—



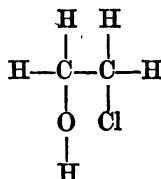
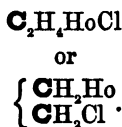
Haloid Ethers of the Dyad Positive Radicals.

As the dihydric alcohols contain two semimolecules of hydroxyl, it follows that there are two classes of haloid ethers derivable from them. The first is formed by the substitution of one of the semimolecules of hydroxyl by chlorine, bromine, &c., and the second by the like displacement of both semimolecules of hydroxyl:—

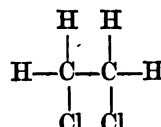
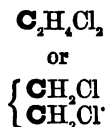
- I. Haloid ethers of the form $C_nH_{2n}HOCl$.
 II. " " " " " $C_nH_{2n}Cl_2$.

The following examples will suffice to illustrate the constitution of both these classes of haloid ethers:—

Chlorhydric glycol or ethy-
lenic chlorhydrate.....



Ethylenic dichloride

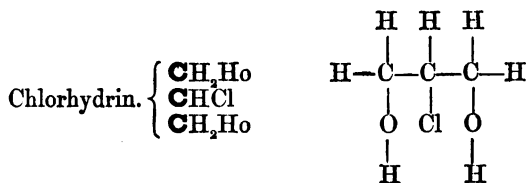


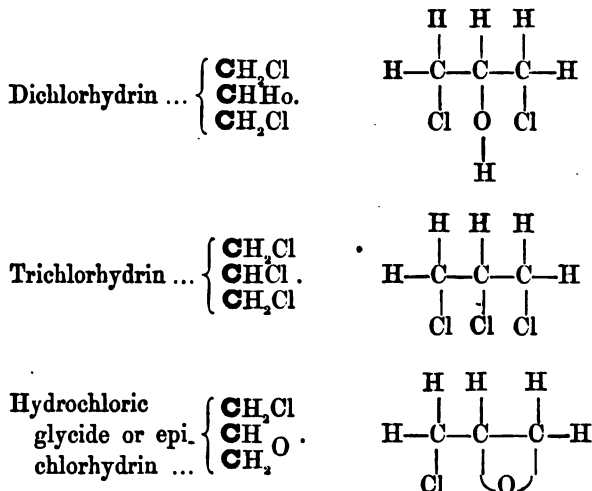
Haloid Ethers of the Triad Positive Radicals.

Three classes of haloid ethers are derived from the trihydric alcohols by the successive substitution of the three semimolecules of hydroxyl contained in these alcohols by chlorine, bromine, &c. A fourth class also exists, which stands intermediate between the ethers and the haloid ethers, and which is formed by the substitution of one of the semimolecules of hydroxyl in the alcohol by a monad negative radical, such as chlorine, bromine, or cyanogen, and the remaining two semimolecules of hydroxyl by a dyad oxygen:—

- I. Haloid ethers of the form $\text{C}_n\text{H}_{2n-1}\text{Ho}_2\text{Cl}$.
- II. " " " $\text{C}_n\text{H}_{2n-1}\text{HoCl}_2$.
- III. " " " $\text{C}_n\text{H}_{2n-1}\text{Cl}_3$.
- IV. " " " $\text{C}_n\text{H}_{2n-1}\text{OCl}$.

The following are examples of each of these classes:—

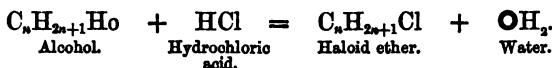




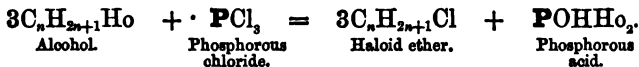
HALOID ETHERS OF THE MONAD POSITIVE RADICALS.

Preparation.—These ethers are produced by the following general reactions :—

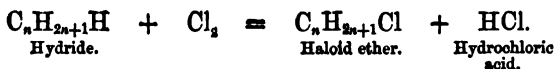
1. By the action of the hydracids upon the alcohols :—



2. By the action of phosphorous chloride on the alcohols :—



3. By the action of chlorine on the hydrides of the radicals :—

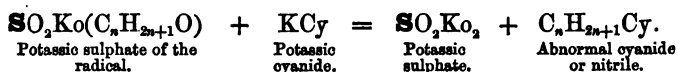


It is obvious that in these reactions bromine and iodine may be used instead of chlorine.

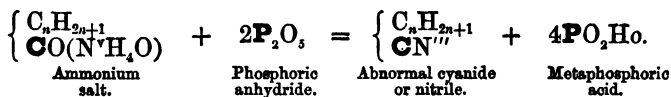
These reactions apply equally to the C_nH_{2n-1} and C_nH_{2n-7} series.

For the preparation of the nitriles, which are isomeric with the cyanides of the radicals, two special reactions (Nos. 1 and 2) are employed.

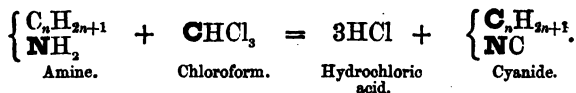
1. The distillation in the dry state of a mixture of the potassic sulphate of the radical with potassic cyanide :—



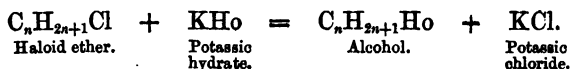
2. The fatty acids are converted into ammonium salts and distilled with phosphoric anhydride, when the abnormal cyanides of the positive radicals which they contain, or nitriles, are produced :—



3. By the action of chloroform on an amine in the presence of an alcoholic solution of potassic hydrate, a normal cyanide is produced. These cyanides are isomeric with those obtained by the two previous processes, and appear to contain nitrogen in the pentad condition :—



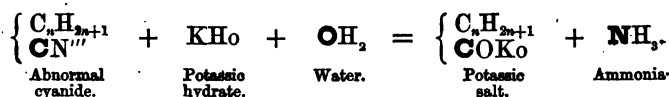
Reactions.—1. Treated with alcoholic solution of potash, most of the haloid ethers of the C_nH_{2n+1} series, except the cyanides, are reconverted into alcohols :—



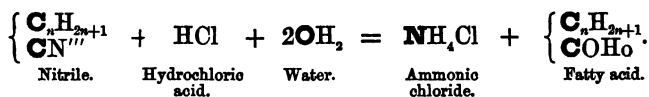
2. The nitriles, or abnormal cyanides, under similar circum-

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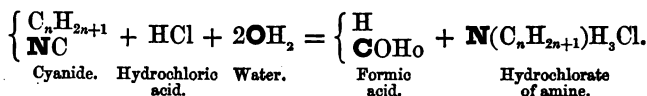
stances are converted into potassic salts of the acids which contain the positive radical of the cyanide :—



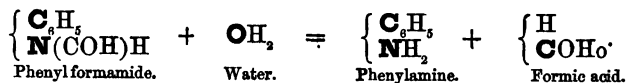
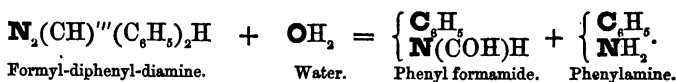
3. The nitriles or abnormal cyanides when submitted to the action of acids yield an ammoniac salt and a fatty acid :—



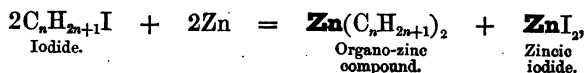
4. The normal cyanides when acted on by acids behave like hydrocyanic acid (see p. 28), producing formic acid and the hydrochlorate of an amine :—



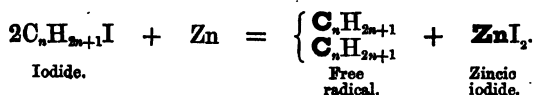
This reaction appears to take place in three stages ; and in the case of phenylic cyanide the intermediate compounds have been obtained :—



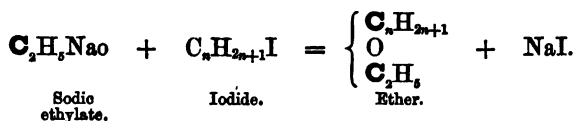
5. When the iodides are digested with zinc or magnesium, the radicals are either liberated or unite with the metal :—



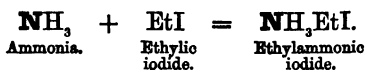
OR



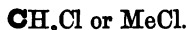
6. When the iodides are submitted to the action of sodic ethylate, a mixed ether (or a simple ether if $n=2$) is formed:—



7. The haloid ethers of the monad positive radicals are the representatives of the hydracids of mineral chemistry, and unite directly with ammonia, producing salts which, when treated with potassic hydrate, yield compound ammonias containing the basylous radical of the haloid ether in the place of one atom of hydrogen:

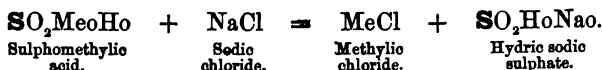
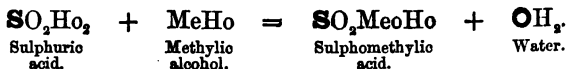


METHYLIC CHLORIDE.



Molecular weight = 50.5. *Molecular volume* $\square\square$. 1 litre of *methyl chloride vapour weighs* 25.25 *oriths*. *Boils at* -21° .

Preparation.—By heating together sodic chloride, methyl alcohol, and sulphuric acid:—



Reaction.—By the action of chlorine, methylic chloride produces three substitution derivatives :—

| | | Boiling-point. |
|------------------------------------|--------------------------|----------------|
| Monochlorinated methylic chloride, | CH_3Cl . | 31° |
| Dichlorinated | " " CHCl_2 . | 60°·8 |
| Trichlorinated | " " CCl_3 . | 78° |

Chloroform, acted on by powdered zinc and a solution of ammonia, produces methylenic dichloride, boiling between 40° and 42°. It seems to differ from monochlorinated methylic chloride, which is said to boil at 31°.

CHLOROFORM, *Dichlorinated Methylic Chloride.*



Molecular weight = 119·5. *Molecular volume* $\square\square$. 1 litre of chloroform vapour weighs 59·75 criths. *Sp. gr.* 1·48. Boils at 60°·8.

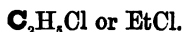
Preparation.—This compound is manufactured in large quantities by heating alcohol with a solution of calcic hypochlorite (*chloride of lime*). It may also be made by treating methylic alcohol in the same manner. For the reaction see p. 57.

Reactions.—1. Chloroform is transformed into potassic formate by boiling with alcoholic potash :—



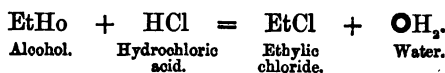
2. When acted upon by chlorine in the presence of sunlight, the hydrogen of chloroform is displaced by chlorine, and carbonic tetrachloride (CCl_4) formed.

ETHYLIC CHLORIDE.

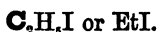


Molecular weight = 64.5. *Molecular volume* $\square\square$. 1 litre of ethylic chloride vapour weighs 32.25 criths. *Sp. gr.* 0.874. Boils at 11°.5.

Preparation.—Ethylic alcohol is saturated with hydrochloric acid, and digested in sealed tubes at 100° for one or two hours, when the mixture separates into two layers, the upper one being the ethylic chloride:—

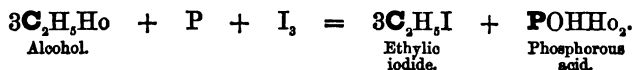


ETHYLIC IODIDE.

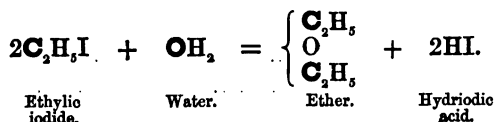


Molecular weight = 156. *Molecular volume* $\square\square$. 1 litre of ethylic iodide vapour weighs 78 criths. *Sp. gr.* 1.9464. Boils at 72°.2.

Preparation.—By placing in a retort two parts by weight of alcohol and one of amorphous phosphorus, and then introducing five parts of iodine and distilling in a water-bath:—



Reaction.—Ethylic iodide, when heated with water in a sealed tube, produces ether and hydriodic acid:—



The methylic and amylic iodides are similar liquids, and obtained by analogous processes; the methylic iodide, CH_3I , has the sp. gr. 2.237, and boils at 42°C . Amylic iodide, $\text{C}_6\text{H}_{11}\text{I}$, has the sp. gr. 1.511, and boils at 146° .

The haloid compounds of the allylic and phenylic series are of comparatively little importance.

HALOID ETHERS OF THE DYAD POSITIVE RADICALS.

I. Haloid ethers of the form $\text{C}_n\text{H}_{2n}\text{HOCl}$.

Preparation.—These ethers are prepared by the action of the hydric acids on the glycols. The following will serve as examples of this class:—

Ethylenic chlorhydrate or chlorhydric glycol $\left\{ \begin{array}{l} \text{CH}_2\text{H}_0 \\ \text{CH}_2\text{Cl} \end{array} \right.$

Ethylenic iodhydrate or iodhydric glycol ... $\left\{ \begin{array}{l} \text{CH}_2\text{H}_0 \\ \text{CH}_2\text{I} \end{array} \right.$

Treated with potassic hydrate, both these bodies give ethylenic oxide, as previously described (p. 90).

II. Haloid ethers of the form $\text{C}_n\text{H}_{2n}\text{Cl}_2$.

Preparation.—These ethers are generally formed by the direct union of the dyad radicals with the negative elements.

The following list comprises the chief members of this class:—

| | | Boiling-point. |
|--------------------------|---|----------------|
| Methylenic chloride..... | CH_2Cl_2 | 40° |
| „ iodide | CH_2I_2 | 181° |
| Ethylenic chloride | $\text{C}_2\text{H}_4\text{Cl}_2$ | 85° |
| „ bromide | $\text{C}_2\text{H}_4\text{Br}_2$ | 129° |

| | | Boiling-point. |
|---------------------------|---|----------------|
| Ethylenic iodide | $\text{C}_2\text{H}_4\text{I}_2$ | — |
| Propylenic chloride | $\text{C}_3\text{H}_5\text{Cl}_2$ | 103° |
| „ bromide | $\text{C}_3\text{H}_5\text{Br}_2$ | 144° |
| „ iodide | $\text{C}_3\text{H}_5\text{I}_2$ | — |
| Butylenic chloride | $\text{C}_4\text{H}_7\text{Cl}_2$ | 127° |
| „ bromide | $\text{C}_4\text{H}_7\text{Br}_2$ | 160° |
| Amylenic chloride | $\text{C}_5\text{H}_9\text{Cl}_2$ | — |
| „ bromide | $\text{C}_5\text{H}_9\text{Br}_2$ | 175° |

By the action of potassium, sodium, or zinc, the radicals are again liberated, except in the case of the methylene compounds. The bromides are the most important members of the series.

ETHYLENIC BROMIDE.



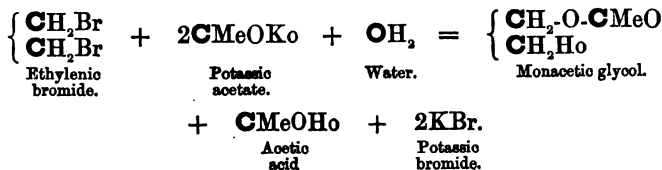
Molecular weight = 188. *Molecular volume* $\square\square$. 1 litre of ethylenic bromide vapour weighs 94 criths. *Sp. gr.* 2.16. *Fuses at* -18° . *Boils at* 129° .

Preparation.—By agitating bromine and water with ethylene.

Reactions.—1. Boiled with alcoholic potash it yields bromethylene or vinylic bromide:—



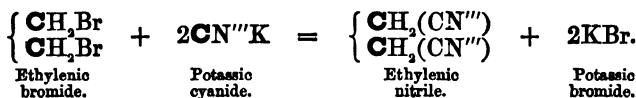
2. Heated with an alcoholic solution of potassic acetate, it yields monacetic glycol.



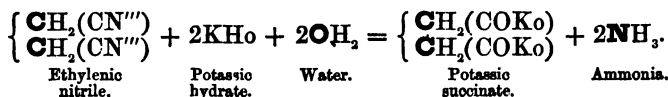
ETHYLENIC CYANIDE, *Ethylenic Nitrile.*

Fuses at 37°.

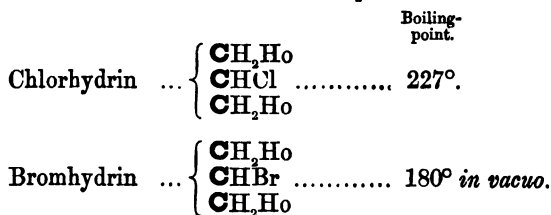
Preparation.—By heating ethylenic bromide with potassic cyanide to 100° for sixteen hours :—



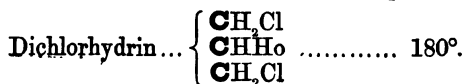
Reaction.—When boiled with alcoholic potash, ethylenic nitrile or abnormal cyanide yields potassic succinate :—

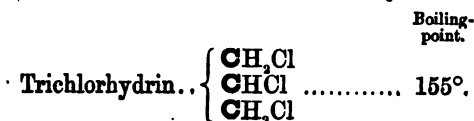
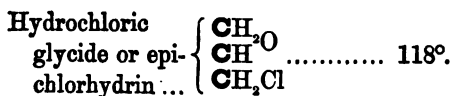
***HALOID ETHERS OF THE TRIAD POSITIVE RADICALS.***

I. of the form $\text{C}_n\text{H}_{2n-1}\text{Ho}_2\text{Cl}$.



II. of the form $\text{C}_n\text{H}_{2n-1}\text{HoCl}_2$.



III. of the form $C_nH_{2n-1}Cl_3$.IV. Of the form $C_nH_{2n-1}OCl$.

Preparation.—The ethers of the first three forms are obtained by the action of the hydracids upon glycerin; whilst those of the fourth are produced by the action of alkalies upon the second form of compounds.

CHAPTER XV.

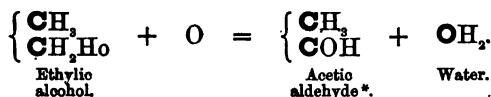
THE ALDEHYDES.

THESE compounds are intermediate between the alcohols and the acids. They are formed from alcohols by the abstraction of hydrogen; hence the name, which is an abbreviation of *alcohol dehydrogenatum*.

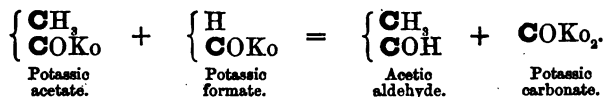
Three series of aldehydes are known, corresponding to the three series of monacid alcohols, viz. :—

- | | |
|----|--|
| A. | Aldehydes derived from $C_nH_{2n+1}Ho$ alcohols. |
| B. | " " " $C_nH_{2n-1}Ho$ " |
| C. | " " " $C_nH_{2n-7}Ho$ " |

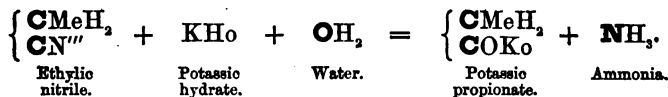
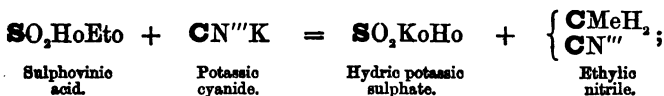
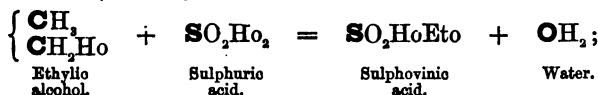
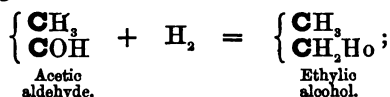
Preparation.—1. The aldehydes are formed by the oxidation of the alcohols; ethylic alcohol, for instance, yields acetic aldehyde :—



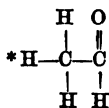
2. Aldehydes are also formed by distilling a mixture of molecular quantities of the potassic salt of a fatty acid and of potassic formate :—



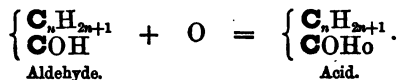
This is an important reaction, as by its means the series of fatty acids can be ascended; for the aldehyde may next be transformed into an alcohol by nascent hydrogen then the alcohol converted into an abnormal cyanide or nitrile, which by treatment with potassic hydrate gives the potassic salt of the next higher acid. Thus :—



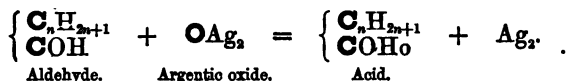
Starting again with potassic propionate, instead of potassic acetate, the same series of reactions can be performed, resulting in potassic butyrate, and so on.



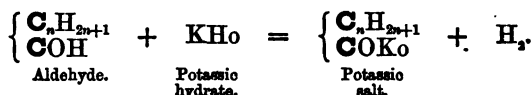
Reactions.—1. By direct absorption of oxygen, the aldehydes are transformed into the corresponding acids :—



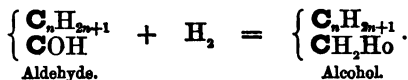
2. Also heated with ammoniacal solution of argentic oxide, the aldehydes are converted into acids, metallic silver being deposited :—



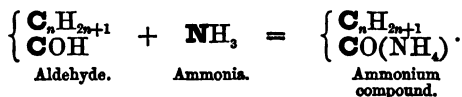
3. When heated with potassic hydrate, the aldehydes yield the potassic salts of the corresponding acids, with evolution of hydrogen :—



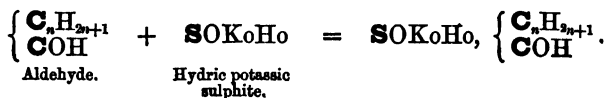
4. Treated with nascent hydrogen, they are converted into the corresponding alcohols :—



5. Most aldehydes combine directly with ammonia, forming crystalline compounds :—



6. Aldehydes also combine with the alkaline hydric sulphites, producing crystalline compounds :—



**A. ALDEHYDES DERIVED FROM THE $C_nH_{2n+1}HO$
SERIES OF ALCOHOLS.**

The following are known:—

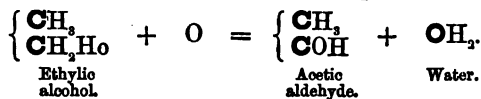
| | | Fusing- point. | Boiling- point. |
|-----------------------|--|-------------------|--------------------|
| Formic aldehyde ... | $\begin{Bmatrix} H \\ COH \end{Bmatrix}$ | — | — |
| Acetic aldehyde | $\begin{Bmatrix} CH_3 \\ COH \end{Bmatrix}$ | — | 21°. |
| Propionic aldehyde.. | $\begin{Bmatrix} CMeH_2 \\ COH \end{Bmatrix}$ or $\begin{Bmatrix} C(CH_3)H_2 \\ COH \end{Bmatrix}$ | — | (40°-45°). |
| Butyric aldehyde ... | $\begin{Bmatrix} CEtH_2 \\ COH \end{Bmatrix}$ or $\begin{Bmatrix} C(C_2H_5)H_2 \\ COH \end{Bmatrix}$ | — | (68°-75°). |
| Valeric aldehyde ... | $\begin{Bmatrix} CPrH_2 \\ COH \end{Bmatrix}$ or $\begin{Bmatrix} C(C_3H_7)H_2 \\ COH \end{Bmatrix}$ | — | 93°. |
| Enanthic aldehyde.. | $\begin{Bmatrix} CA_7H_2 \\ COH \end{Bmatrix}$ or $\begin{Bmatrix} C(C_5H_{11})H_2 \\ COH \end{Bmatrix}$ below -12°. | | 152°. |
| Capric aldehyde..... | $\begin{Bmatrix} C(C_8H_{17})H_2 \\ COH \end{Bmatrix}$ | - 2°. | 228°? |
| Euodic aldehyde..... | $\begin{Bmatrix} C(C_9H_{19})H_2 \\ COH \end{Bmatrix}$ | + 7°. | 213°. |
| Lauric aldehyde | $\begin{Bmatrix} C(C_{10}H_{21})H_2 \\ COH \end{Bmatrix}$ | — | 232°. |
| Palmitic aldehyde ... | $\begin{Bmatrix} C(C_{15}H_{31})H_2 \\ COH \end{Bmatrix}$ | 52°. | |

ACETIC ALDEHYDE, *Aldehyde*.



Molecular weight = 44. *Molecular volume* $\square\square$. 1 litre of aldehyde vapour weighs 22 criths. *Sp. gr.* = 0.79. Boils at 21°.8.

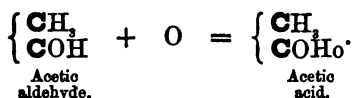
Preparation.—1. By oxidizing alcohol with chromic acid, chlorine water, or manganic oxide and sulphuric acid:—



2. By oxidation, casein, fibrin, and albumen also yield aldehyde.

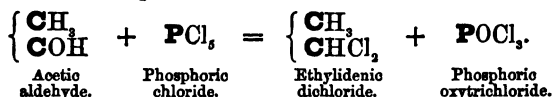
3. Aldehyde is formed when the vapour of alcohol or ether is passed through a tube heated to dull redness.

Reactions.—1. It gradually absorbs oxygen from the air, forming acetic acid, into which it is also readily converted by oxidizing agents:—



2. It reduces silver salts, depositing lustrous metallic silver on the sides of the vessel.

3. By the action of phosphoric chloride on aldehyde, ethylenic dichloride is produced:—

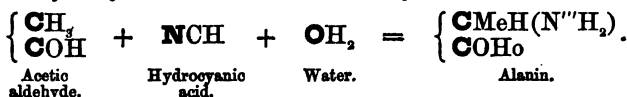


4. When submitted to the action of potassium, one atom of hydrogen is substituted by an atom of the metal, the compound

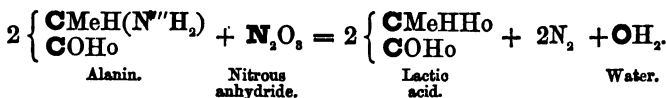


being formed.

5. Hydrocyanic acid transforms aldehyde into alanin:—



By the action of nitrous anhydride, alanin or lactamic acid is converted into lactic acid:—



There are three isomeric modifications of aldehyde:—

Metaldehyde, crystalline, subliming at 120°.

Paraldehyde, liquid, boiling at 125°.

Elaldehyde, crystalline, fusing at 2°, boiling at 94°.

By the action of chlorine upon alcohol, trichlor-aldehyde is formed containing 3 atoms of chlorine in the place of 3 atoms of methylic hydrogen. It is named *chloral*,



This compound immediately unites with one molecule of water, forming *chloral hydrate*, which has the following constitutional formula:—



In the same operation *chloral alcoholate* is generally produced. Its constitution is expressed by the following formula:—



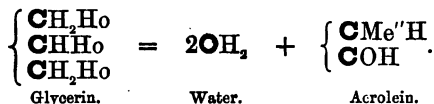
B. ALDEHYDES DERIVED FROM THE $C_nH_{2n-1}HO$ ALCOHOLS.

ACROLEIN. *Acrylic Aldehyde.*

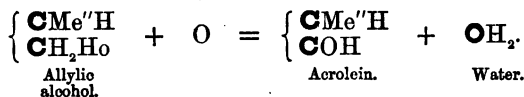


Molecular weight = 56. *Molecular volume* $\square\square$. 1 litre of acrolein vapour weighs 28 criths. Boils at $52^{\circ}4$.

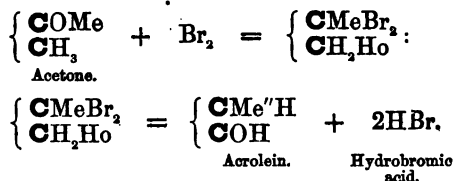
Preparation.—1. By the action of phosphoric anhydride or of sulphuric acid on glycerin :—



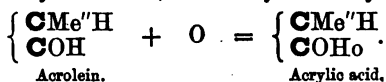
2. By the oxidation of allylic alcohol :—



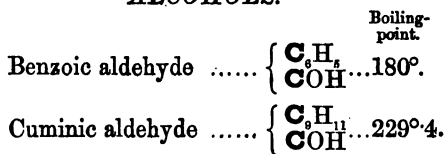
3 By the action of heat on the product of the union of acetone with bromine :—



Reaction.—By oxidation, acrolein yields acrylic acid :—



C. ALDEHYDES DERIVED FROM THE $\text{C}_n\text{H}_{2n-7}\text{Ho}$ ALCOHOLS.



BENZOIC ALDEHYDE, *Oil of Bitter Almonds, Hydride of Benzoyl.*

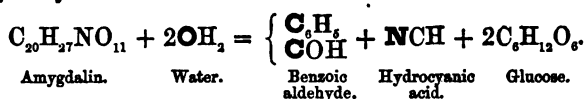


Molecular weight = 106. *Molecular volume* $\square\square$. 1 litre of benzoic aldehyde vapour weighs 53 criths. *Sp. gr.* 1·043. Boils at 180°.

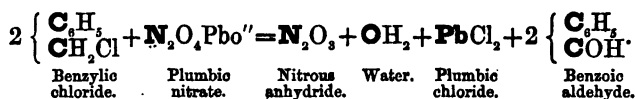
Preparation.—1. By the oxidation of amygdalin by nitric acid, and by the action of a mixture of manganic oxide and sulphuric acid on albumen, fibrin, casein, and gelatin.

2. By digesting bitter almonds with water for five or six hours at 30°–40°. The synaptase present acts as a ferment on

the amygdalin, converting it into glucose, benzoic aldehyde, and hydrocyanic acid :—

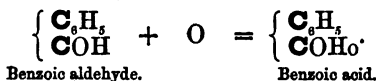


3. By digesting together plumbic nitrate, water, and benzylic chloride (chlorotoluol), benzoic aldehyde is formed :—

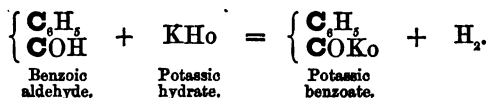


The benzylic chloride is prepared by passing chlorine into the vapour of boiling toluol.

Reactions.—1. When exposed to the air, benzoic aldehyde absorbs oxygen and is converted into benzoic acid :—



2. Heated with solid potassic hydrate, it gives hydrogen and potassic benzoate :—



CHAPTER XVI.

THE ACIDS.

THE acids form the most numerous family of organic compounds.

Many of them are contained in plants in the free state, or in combination as metallic or ethereal salts.

Others are produced by the action of chemical agents on various organic substances.

Some are formed in the animal organism, as, for instance, formic, paralactic, oleic, and stearic acids.

The organic acids are divided into three great classes, according to their basicity :—

1. Monobasic acids.
2. Dibasic acids.
3. Tribasic acids.

The basicity of organic acids is determined by the following simple law :—*an organic acid containing n semimolecules of oxatyl is n-basic.*

MONOBASIC ACIDS.

The monobasic acids, which always contain a single semimolecule of oxatyl (COHo), include the six following series :—

General formulæ.

- | | |
|----------------------------------|---|
| 1. Acetic or fatty series | $\left\{ \begin{array}{l} \text{C}_n\text{H}_{2n+1} \\ \text{COHo} \end{array} \right.$ |
| 2. Acrylic or oleic series | $\left\{ \begin{array}{l} \text{C}(\text{C}_n\text{H}_{2n})''(\text{C}_m\text{H}_{2m+1}) \\ \text{COHo} \end{array} \right.$ |
| 3. Lactic series | $\left\{ \begin{array}{l} \text{C}(\text{C}_n\text{H}_{2n+1})(\text{C}_m\text{H}_{2m+1})\text{Ho} \\ \text{COHo} \end{array} \right.$ |
| 4. Pyruvic series | $\left\{ \begin{array}{l} \text{CO}(\text{C}_n\text{H}_{2n+1}) \\ \text{COHo} \end{array} \right.$ |
| 5. Glyoxylic series | $\left\{ \begin{array}{l} \text{C}(\text{C}_n\text{H}_{2n+1})\text{Ho}_2 \\ \text{COHo} \end{array} \right.$ |
| 6. Benzoic or aromatic series | $\left\{ \begin{array}{l} \text{C}_n\text{H}_{2n-7} \\ \text{COHo} \end{array} \right.$ |

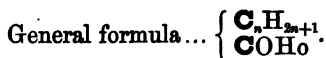
The 1st, 2nd, 3rd, 5th, and 6th of these series may be regarded as the derivatives from corresponding series of alcohols.

1. The Acetic series from the Methyl series of alcohols.
2. " Acrylic " " Vinyl " "
3. " Lactic " " Glycol " "
5. " Glyoxylic " " Glycerin " "
6. " Benzoic " " Phenyl " "

The acids of the first, second, fourth, and sixth series are termed *monohydric* as well as monobasic; whilst the acids of the third series are termed *dihydric* and monobasic, indicating their origin from the dihydric alcohols, and that they contain two semimolecules of hydroxyl, one of which is in the oxatyl or negative part, and the other in the positive part of the molecule. The hydrogen of the latter hydroxyl may be displaced by highly positive metals, in the same manner as the hydrogen of the hydroxyl in alcohols; but it cannot be displaced by double decomposition with bases, in the same manner as the hydrogen in the oxatyl may be substituted.

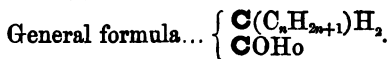
The acids of the fifth series are termed *trihydric* and monobasic, indicating that they are derived from the trihydric alcohols, and that they contain, besides the hydroxyl in the oxatyl, two other semimolecules of hydroxyl in the positive part of the molecule.

1. ACETIC OR FATTY SERIES OF ACIDS.

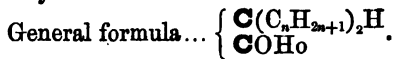


These acids may be conveniently arranged under three divisions, viz.:—

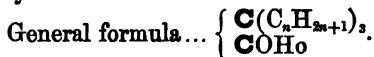
A. Normal acids.



B. Secondary acids.



C. Tertiary acids.



A. NORMAL ACIDS OF THE ACETIC OR FATTY SERIES.



In formic acid, which is generally considered to be the first term of this division, the radical $\mathbf{C}(\mathbf{C}_n\mathbf{H}_{2n+1})\mathbf{H}_2$ is replaced by \mathbf{H} ; and in acetic acid the value of $n=0$. In reference to the following list of normal fatty acids, it must be borne in mind that the normal character has not been established in the case of those members which possess a higher molecular weight than œnanthylic acid:—

| | | Fusing point. | Boiling-point. |
|-----------------------|---|----------------|----------------|
| Formic acid..... | $\left\{ \begin{array}{l} \mathbf{H} \\ \mathbf{COH}_o \end{array} \right.$ | +1°. | 100°. |
| Acetic acid | $\left\{ \begin{array}{l} \mathbf{Me} \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{CH}_3 \\ \mathbf{COH}_o \end{array} \right.$ | +17°. | 117°. |
| Propionic acid ... | $\left\{ \begin{array}{l} \mathbf{CMeH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{CH}_3)\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | — | 141°. |
| Butyric acid | $\left\{ \begin{array}{l} \mathbf{CEtH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{C}_2\mathbf{H}_5)\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | below -20°. | 161°. |
| Valeric acid | $\left\{ \begin{array}{l} \mathbf{CPrH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{C}_3\mathbf{H}_7)\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | — | 175°. |
| Isopropacetic acid | $\left\{ \begin{array}{l} \mathbf{C}\beta\mathbf{PrH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{CMe}_2\mathbf{H})\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | — | 175°. |
| Caproic acid | $\left\{ \begin{array}{l} \mathbf{CBuH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{C}_4\mathbf{H}_9)\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | +5°. | 198°. |
| œNanthylic acid | $\left\{ \begin{array}{l} \mathbf{CAyH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{C}_5\mathbf{H}_{11})\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | — | 212°. |
| Caprylic acid ... | $\left\{ \begin{array}{l} \mathbf{CCpH}_2 \\ \mathbf{COH}_o \end{array} \right.$ or $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{C}_6\mathbf{H}_{13})\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | +14°. | 236°. |
| Pelargonic acid | $\left\{ \begin{array}{l} \mathbf{C}(\mathbf{C}_7\mathbf{H}_{15})\mathbf{H}_2 \\ \mathbf{COH}_o \end{array} \right.$ | +18°f | 260°. |

| | | Fusing-point. |
|-----------------------|--|---------------|
| Capric acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_8\text{H}_{17})\text{H}_2 \\ \text{O} \text{H}_\text{o} \end{array} \right.$ | 27°·2(30°). |
| Lauric acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{10}\text{H}_{21})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 43°·6. |
| Myristic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{12}\text{H}_{25})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 53°·8. |
| Palmitic acid..... | $\left\{ \begin{array}{l} \text{C}(\text{C}_{14}\text{H}_{29})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 62°. |
| Margaric acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{15}\text{H}_{31})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 59°·9 ? |
| Stearic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{16}\text{H}_{33})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 69°·2. |
| Arachidic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{18}\text{H}_{37})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 75°. |
| Behenic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{20}\text{H}_{41})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 76°. |
| Hyœnasic acid..... | $\left\{ \begin{array}{l} \text{C}(\text{C}_{22}\text{H}_{47})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 77°. |
| Cerotic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{24}\text{H}_{49})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 78°. |
| Melissic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{26}\text{H}_{57})\text{H}_2 \\ \text{C} \text{O} \text{H}_\text{o} \end{array} \right.$ | 88°. |

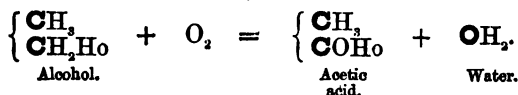
Occurrence.—The greater number of the acids of this series are met with already formed in nature, some in the free state, as formic acid in ants and nettles, valeric acid in the valerian root, pelargonic acid in the essential oil of the *Pelargonium roseum*, and cerotic acid in bee's-wax.

Others are met with as the ethereal salts of monohydric alcohols. Thus spermaceti is cetylic palmitate, and chinese wax cerylic cerotate.

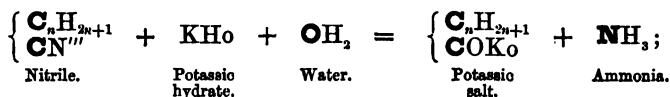
A large number exist as natural fats in the form of the ethereal salts of glycerin: this is the case with butyric, pal-

mitic, and stearic acids, which, united with glycerin, form respectively butyrin, palmitin, and stearin.

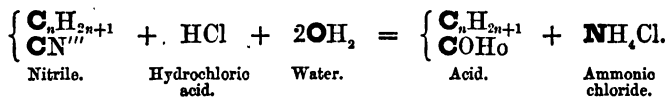
Formation.—1. By the oxidation of the normal alcohols of the methyl series, as in the conversion of alcohol into acetic acid by heating it with a solution of chromic acid:—



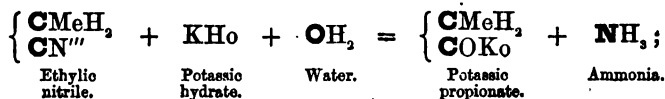
2. By the action of alkalies or acids upon the nitriles or abnormal cyanides of the $\text{C}_n\text{H}_{2n+1}$ series of radicals:—



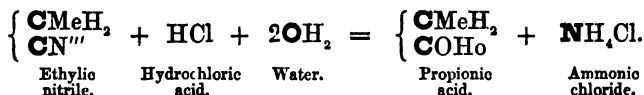
and



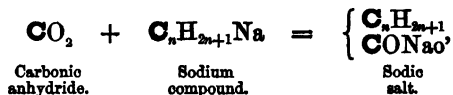
Instances of these reactions are seen in the treatment of ethylic nitrile by a boiling solution of potassio hydrate, when it is converted into potassio propionate, ammonia being evolved, thus—



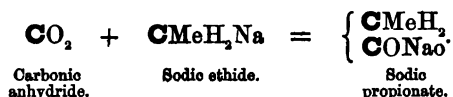
and in the conversion of ethylic nitrile, by the action of hydrochloric acid, into ammonio chloride and propionic acid—



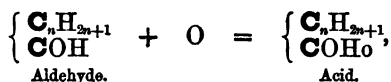
3. By the action of the potassium or sodium compounds of the C_nH_{2n+1} radicals upon carbonic anhydride—



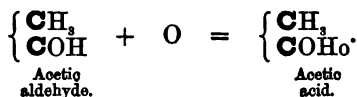
as, for example, in the formation of sodic propionate by the absorption of carbonic anhydride by sodic ethide:—



4. By the oxidation of aldehydes—



as in the conversion of acetic aldehyde into acetic acid by the absorption of atmospheric oxygen:—



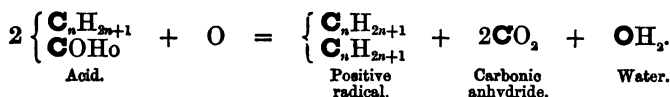
Besides these reactions of general application, there are numerous special methods for the production of certain members of this series. In most of these methods, however, the reactions cannot be clearly traced.

Thus, by the oxidation of albumen, fibrin, casein, and other similar substances, there are produced formic, acetic, propionic, butyric, valeric, and caproic acids.

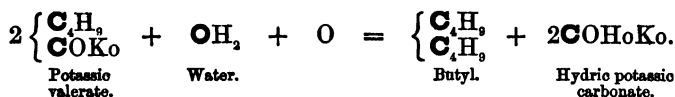
Propionic and butyric acids are produced in some kinds of fermentation; and acetic acid is obtained by the destructive distillation of wood and other similar substances.

Relations of the Normal Fatty Acids to the C_nH_{2n+1} Series of Radicals.

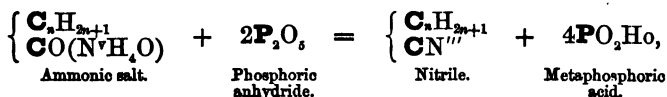
1. When these acids are submitted to the action of nascent oxygen evolved by electrolysis, the negative radical oxatyl is converted into carbonic anhydride and water, the positive radical being set at liberty :—



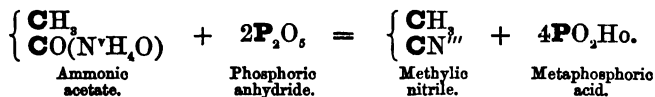
On electrolyzing a solution of potassic valerate, hydric potassic carbonate and the normal radical butyl are formed :—



2. When the ammonic salts of these acids are heated with phosphoric anhydride, they are converted into the nitriles or abnormal cyanides of the radicals of the C_nH_{2n+1} series—



as in the transformation of ammonic acetate into methylic nitrile by distillation with phosphoric anhydride :—



These abnormal cyanides are converted into monohydric alcohols by Mendius's reaction (see p. 55).

From the alcohols so obtained, the C_nH_{2n+1} radicals are isolated as described at page 53.

Relations of the Normal Fatty Acids to the $C_nH_{2n+1}HO$ Series of Alcohols.

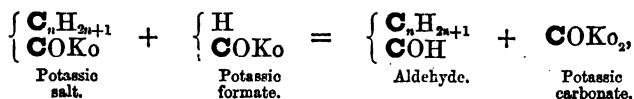
1. By oxidation the normal alcohols yield these acids, as above shown.

2. Conversely, the normal fatty acids can be converted into the $C_nH_{2n+1}HO$ alcohols,—

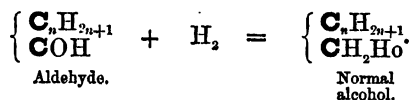
1st, by Mendius's reaction (see p. 55);

2nd, by Piria and Wurtz's reactions, viz. :—

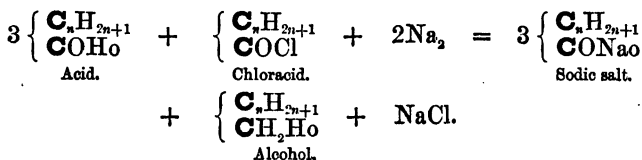
Distillation of the potassic salt of the fatty acid with an equivalent quantity of potassic formate, by which the acid is converted into the aldehyde,



and subsequent treatment of the aldehyde by nascent hydrogen,



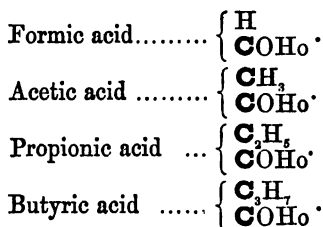
3. By the action of sodium amalgam upon a mixture of the acid and chloracid :—



The anhydride of the acid is also formed and converted, by the nascent hydrogen evolved by the action of the sodium upon the acid, into alcohol.

Relations of the Normal Fatty Acids to each other. Ascent of the Series.

If the hydrogen constituting the positive part of formic acid were substituted successively by methyl, ethyl, &c., the whole series of normal fatty acids would be obtained :—



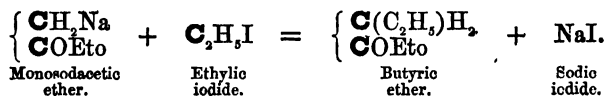
This substitution has not yet been accomplished; but an analogous series of reactions has been effected with acetic acid.

By the action of sodium on acetic ether, one of the hydrogen atoms in the positive part of the compound becomes substituted by sodium, producing

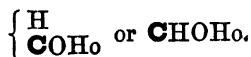


By acting on this body with the iodides of the $\text{C}_n\text{H}_{2n+1}$ radicals, ethylic salts of the higher acids are produced.

On submitting monosodacetic ether to the action of ethylic iodide, for instance, butyric ether is produced—



FORMIC ACID.



Molecular weight = 46. *Molecular volume* $\square\square$. 1 litre of formic acid vapour weighs 23 criths. *Sp. gr. of liquid* 1.2353. *Fuses at* 1° C. *Boils at* 100° C.

Occurrence.—If red ants be made to pass over blue litmus-paper and be at the same time irritated, they leave a red streak behind them, produced by the formic acid which they eject. By placing the hand on an ant-hill, a tingling sensation is felt from the same cause, and the hand acquires the powerful and pleasant odour of formic acid.

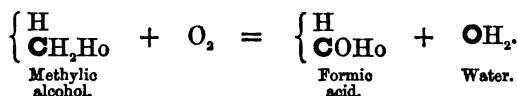
Formic acid also occurs in the hairs of certain caterpillars and in the sting of nettles.

Formation.—1. Formic acid is produced in a very large number of chemical reactions, as in the oxidation of many organic bodies (such as starch, woody fibre, or tartaric acid) by a mixture of sulphuric acid and manganic oxide, or by potassic hydrate or chromic acid.

2. By the action of potassic hydrate on chloroform, potassic formate is generated:—



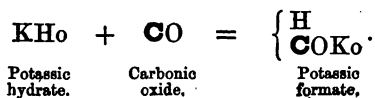
3. By the oxidation of methylic alcohol:—



4. By heating equal weights of dry oxalic acid and glycerin together to 75° C., when the oxalic acid splits into formic acid and carbonic anhydride:—

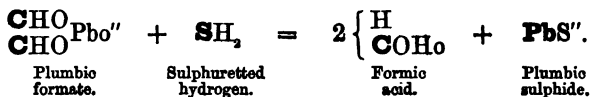


5. By digesting together at 100°, for forty-eight hours, potassic hydrate and carbonic oxide:—

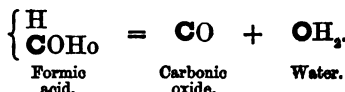


6. Formic acid is produced in small quantities by digesting carbon with permanganic acid.

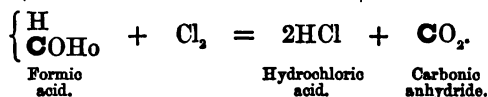
Formic acid from any of these sources is obtained in the concentrated state by decomposing plumbic formate with sulphuretted hydrogen, and afterwards rectifying the acid over plumbic formate:—



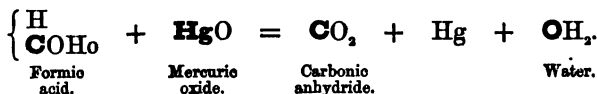
Character.—When heated with concentrated sulphuric acid, formic acid splits into water and carbonic oxide:—



Chlorine converts formic acid into hydrochloric acid and carbonic anhydride:—



When heated with excess of mercuric oxide, it is converted into carbonic anhydride and water, the mercury being reduced to the metallic state:—



ACETIC ACID.

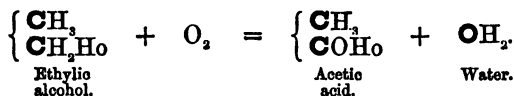


Molecular weight = 60. *Molecular volume* $\square\square$. 1 litre of acetic acid vapour weighs 30 criths. *Sp. gr. of liquid* 1.064. *Fuses at* +17°. *Boils at* 117°.

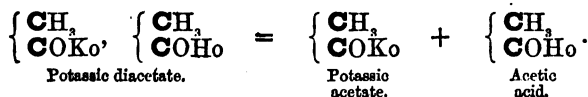
Occurrence.—Found in small quantities in the juices of plants and in animal fluids.

Manufacture.—1. By the destructive distillation of wood, a liquid is obtained which contains acetic acid; the acid is purified by being converted first into a calcic, and then into a sodic salt, the latter being afterwards decomposed by sulphuric acid.

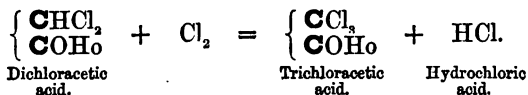
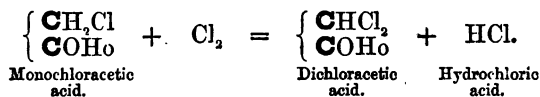
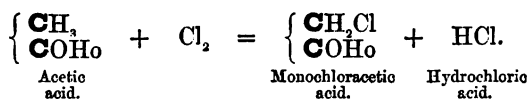
2. By the oxidation of ethylic alcohol:—



Preparation.—Pure acetic acid may be obtained by distilling potassic diacetate:—



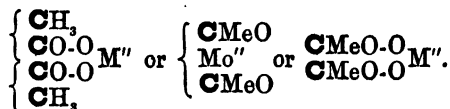
Character.—Chlorine acts on acetic acid in sunlight, producing three chlorinated acids, in which chlorine is substituted for hydrogen:—



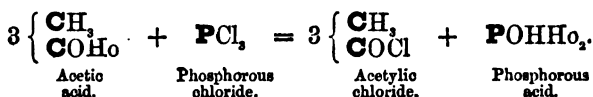
The salts of acetic acid in which the hydrogen of the oxatyl is replaced by monad metals have the general formula



The acetates of the dyad metals have the constitution represented by the following general formula :—



By the action of phosphorous chloride, acetic acid yields acetylic chloride :—



PROPIONIC ACID, *Methacetic Acid*.



Molecular weight = 74. *Molecular volume* $\square\square$. 1 litre of propionic acid vapour weighs 37 criths. Boils at 141°.

Preparation.—1. By the oxidation of metacetone—a liquid obtained by the distillation of a mixture of sugar and lime.

2. By the action of concentrated solution of potassic hydrate on sugar.

3. By the fermentation of glycerin, and also of sugar, by means of putrid cheese in the presence of calcic carbonate.

4. By the action of potassic hydrate or hydrochloric acid on abnormal ethylic cyanide (see p. 117).

5. By the action of carbonic anhydride on sodic ethide (see p. 118).

6. By the action of hydriodic acid on lactic acid :—



BUTYRIC ACID, Ethacetic Acid.

Molecular weight = 88. *Molecular volume* $\square\square$. 1 litre of butyric acid vapour weighs 44 criths. *Sp. gr. of liquid* 0.9886. *Fuses below* -20° . *Boils at* 161°C .

Occurrence.—In butter, juice of flesh, perspiration, and many animal secretions.

Preparation.—1. By the fermentation of sugar with putrid cheese.

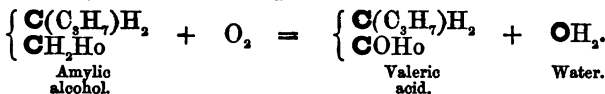
2. By the action of ethylic iodide on sodacetic ether (for reaction, see page 121).

VALERIC ACID, Valerianic Acid.

Molecular weight = 102. *Molecular volume* $\square\square$. 1 litre of valeric acid vapour weighs 51 criths. *Sp. gr. of liquid* 0.937. *Boils at* 175° .

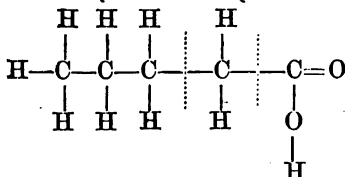
Occurrence.—In many plants, as in the roots of valerian and angelica.

Preparation.—By the oxidation of amylie alcohol with a mixture of sulphuric acid and dipotassic dichromate:—

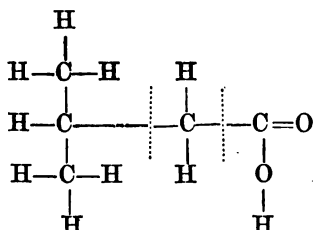


Isomeric forms.—There are four possible isomers of valeric acid:—

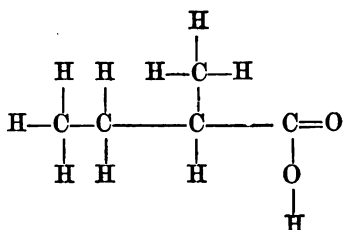
Normal valeric acid or $\begin{cases} \text{C}^{\text{Pr}}\text{H}_2 \\ \text{COH}^{\text{o}} \end{cases}$ or $\begin{cases} \text{CH}_2(\text{CH}_2[\text{CH}_2(\text{CH}_3)]) \\ \text{COH}^{\text{o}} \end{cases}$.
propacetic acid



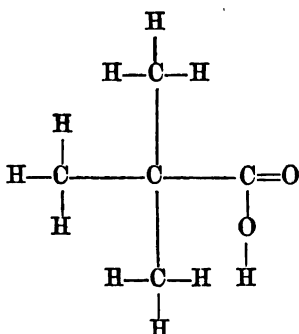
Isopropacetic acid ... $\left\{ \begin{array}{l} \text{CPr}\beta\text{H}_2 \\ \text{COH}_\alpha \end{array} \right.$ or $\left\{ \begin{array}{l} \text{CH}[\text{CH}(\text{CH}_3)_2] \\ \text{COH}_\alpha \end{array} \right.$



Methethacetic acid... $\left\{ \begin{array}{l} \text{CEtMeH} \\ \text{COH}_\alpha \end{array} \right.$ or $\left\{ \begin{array}{l} \text{CH}(\text{CH}_3)[\text{CH}_2(\text{CH}_3)] \\ \text{COH}_\alpha \end{array} \right.$

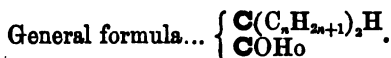


Trimethacetic acid ... $\left\{ \begin{array}{l} \text{CMe}_3 \\ \text{COH}_\alpha \end{array} \right.$ or $\left\{ \begin{array}{l} \text{C}(\text{CH}_3)_3 \\ \text{COH}_\alpha \end{array} \right.$



Of these, the normal, the isopropacetic, and the trimethacetic acid are known.

B. SECONDARY FATTY ACIDS.



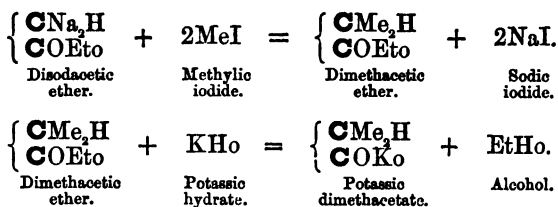
Formation.—1. By the action of the iodides of the $\text{C}_n\text{H}_{2n+1}$ radicals on disodacetic ether, the ethereal salts of these acids are produced.

2. By the action of a boiling solution of caustic potash upon the nitriles or abnormal cyanides of the secondary radicals.

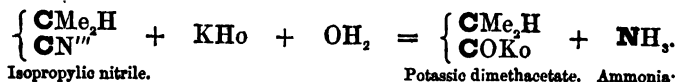
DIMETHACETIC ACID, or *Isobutyric Acid*.

Molecular weight = 88. *Molecular volume* $\square\square$. 1 litre of dimethacetic acid vapour weighs 44 criths. Boils at 152° . Isomeric with butyric or ethacetic acid.

Preparation.—1. As a potassic salt, by the action of methylic iodide on disodacetic ether and the subsequent decomposition, by alcoholic solution of potash, of the ethereal salt so formed:—



2. By boiling isopropyl nitrile with solution of caustic potash:—



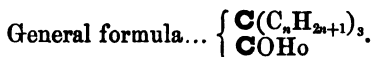
Reaction.—By a hot solution of chromic acid dimethacetic acid is decomposed into carbonic anhydride and acetic acid :—



Acetone is sometimes formed as an intermediate product.

Diethacetic acid, $\left\{ \begin{array}{c} \text{CEt}_2\text{H} \\ \text{COH}_o \end{array} \right.$, isomeric with caproic acid, and
diamylacetic acid, $\left\{ \begin{array}{c} \text{CAy}_2\text{H} \\ \text{COH}_o \end{array} \right.$, isomeric with lauric acid, have been prepared by the substitution of ethylic and amyl iodides in the above reaction.

C. TERTIARY FATTY ACIDS.



Formation.—As ethereal salts, by the action of the iodides of the $\text{C}_n\text{H}_{2n+1}$ radicals on trisodacetic ether.

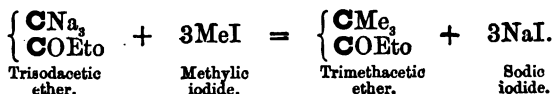
TRIMETHACETIC ACID.



Molecular weight = 102. *Molecular volume* $\square\square$. 1 litre of trimethacetic acid vapour weighs 51 criths. Isomeric with valeric acid.

For the graphic formula of trimethacetic acid see p. 127.

Preparation.—As an ethereal salt, by the action of methylic iodide on trisodacetic ether :—



CHAPTER XVII.

THE ACIDS.

2. ACRYLIC OR OLEIC SERIES OF ACIDS.

General formula of normal and secondary acids $\left\{ \begin{array}{l} \text{C}(\text{C}_n\text{H}_{2n})''(\text{C}_m\text{H}_{2m+1}) \\ \text{COH}_o \end{array} \right.$

This series is divided into normal, secondary, and olefine acids. In the normal acids $m=0$; in the secondary it must be a positive integer.

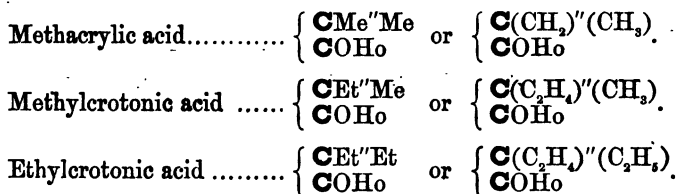
Most of the normal acids exist as ethereal salts of glycerin in natural fats and oils.

The following is a list of the acrylic series of acids:—

A. NORMAL ACIDS.

| | | | | | |
|---|---|-------|---|--|--|
| Acrylic acid | $\left\{ \begin{array}{l} \text{CMe}''\text{H} \\ \text{COH}_o \end{array} \right.$ | or | $\left\{ \begin{array}{l} \text{C}(\text{CH}_2)''\text{H} \\ \text{COH}_o \end{array} \right.$ | | |
| Crotonic acid..... | $\left\{ \begin{array}{l} \text{CEt}''\text{H} \\ \text{COH}_o \end{array} \right.$ | or | $\left\{ \begin{array}{l} \text{C}(\text{C}_2\text{H}_5)''\text{H} \\ \text{COH}_o \end{array} \right.$ | | |
| Angelie acid | $\left\{ \begin{array}{l} \text{CPr}''\text{H} \\ \text{COH}_o \end{array} \right.$ | or | $\left\{ \begin{array}{l} \text{C}(\text{C}_3\text{H}_7)''\text{H} \\ \text{COH}_o \end{array} \right.$ | | |
| Pyroterebic acid | $\left\{ \begin{array}{l} \text{CBu}''\text{H} \\ \text{COH}_o \end{array} \right.$ | or | $\left\{ \begin{array}{l} \text{C}(\text{C}_4\text{H}_9)''\text{H} \\ \text{COH}_o \end{array} \right.$ | | |
| Damaluric acid | $\text{C}_7\text{H}_{12}\text{O}_2$ | | | | |
| Damolic acid | $\text{C}_{13}\text{H}_{24}\text{O}_2$ | | | | |
| Moringic acid..... | } | | $\text{C}_{15}\text{H}_{28}\text{O}_2$ | | |
| Cimicic acid | | | | | |
| Phytotoleic acid..... | } | | $\text{C}_{16}\text{H}_{30}\text{O}_2$ | | |
| Hypogæic acid | | | | | |
| Gaidic acid..... | | | | | |
| Oleic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_{16}\text{H}_{32})''\text{H} \\ \text{COH}_o \end{array} \right.$ | | | | |
| Elaidic acid..... | $\text{C}_{18}\text{H}_{34}\text{O}_2$ | | | | |
| Doeglic acid | $\text{C}_{19}\text{H}_{36}\text{O}_2$ | | | | |
| Brassic acid. (<i>Erucic</i> acid) | $\text{C}_{22}\text{H}_{42}\text{O}_2$ | | | | |

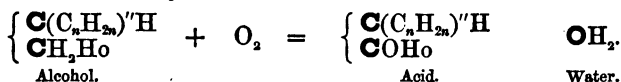
B. SECONDARY ACIDS.



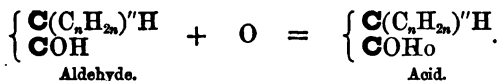
C. OLEFINE ACIDS.



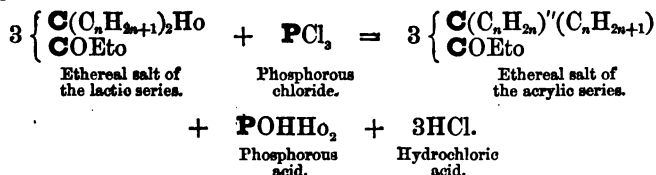
Formation of Normal Acids.—1. By the oxidation of the alcohols of the vinyl or $\text{C}_n\text{H}_{2n-1}\text{Ho}$ series:—



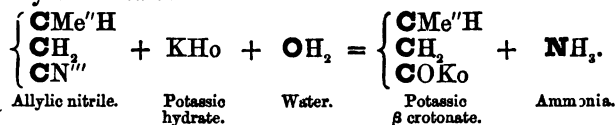
2. By the oxidation of the aldehydes of the acrolein or $\left\{ \begin{array}{l} \text{C}(\text{C}_n\text{H}_{2n})''\text{H} \\ \text{COH} \end{array} \right.$ series:—



Formation of Secondary Acids.—By the action of phosphorous chloride, phosphoric chloride, phosphoric oxytrichloride or phosphoric anhydride upon the ethereal salts of secondary acids of the lactic series, the elements of water are removed and the ethereal salts of the acrylic secondary division of acids produced:—

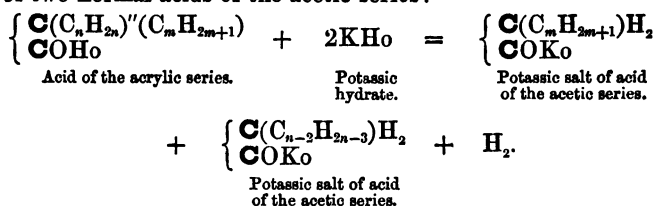


Formation of Olefine Acids.—By the action of potassic hydrate upon the nitriles or abnormal cyanides of the C_nH_{2n-1} family of radicals:—

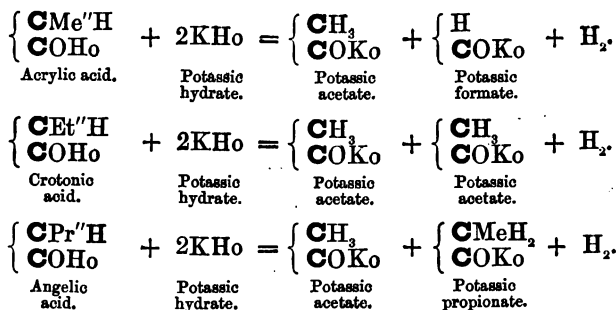


Relations of the Acrylic to the Acetic Series of Acids.

The normal and secondary acids of the acrylic series, when treated with fused potassic hydrate, yield the potassic salts of two normal acids of the acetic series:—



All the members of the acrylic series found in nature give acetic acid as one of the acids produced in this reaction. From this and other considerations, it is believed that their positive radicals all contain one atom of hydrogen and a dyad radical. They are normal acids; and by the action of fused potassic hydrate the dyad radical becomes substituted by two atoms of hydrogen. Thus:—



Some of the secondary acids also give acetic acid when treated with fused potassic hydrate; but this can only happen when the dyad radical is ethylene, thus:—

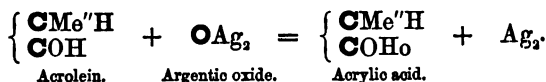


ACRYLIC ACID.

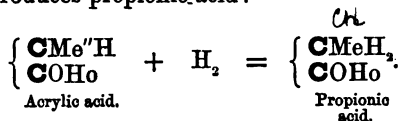


Molecular weight = 72. *Boils at about* 100°.

Preparation.—By the oxidation of acrolein with argentic oxide:—

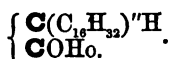


Reactions.—1. Acrylic acid, under the influence of nascent hydrogen, produces propionic acid:—



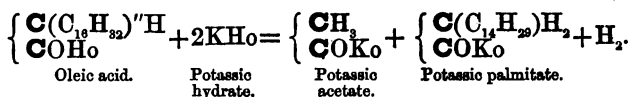
2. Acrylic acid also combines directly with bromine, producing dibromopropionic acid.

OLEIC ACID.



Preparation.—Obtained in the purification of stearic acid.

Reaction.—Heated with potassic hydrate, it gives potassic acetate and palmitate :—

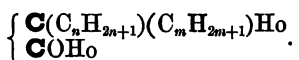


CHAPTER XVIII.

THE ACIDS.

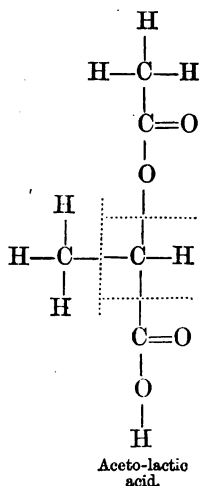
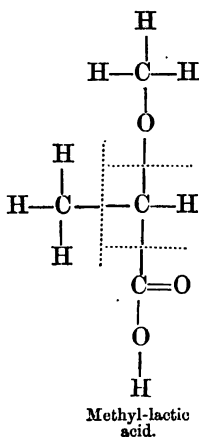
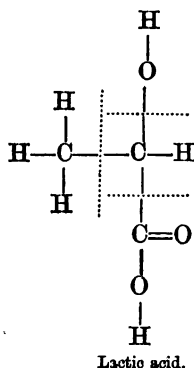
3. LACTIC SERIES OF ACIDS.

General formula of normal and secondary acids :—



In the normal acids m in this formula = 0; but in the secondary acids it must be a positive integer.

The members of the lactic series may be defined as acids containing one semimolecule of oxatyl, the fourth bond of the carbon of which is united with the carbon of a positive group containing one semimolecule of hydroxyl, or of the peroxide of a monad organic radical either positive or negative. The following examples will serve to illustrate this definition :—



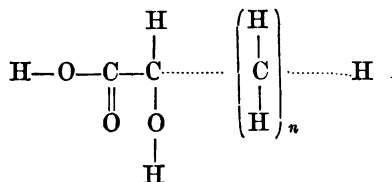
The acids of this series at present known, or which could be obtained by obvious processes, are classified into the following eight divisions :—

1. Normal Acids.
2. Etheric Normal Acids.
3. Secondary Acids.
4. Etheric Secondary Acids.
5. Normal Olefine Acids.
6. Etheric Normal Olefine Acids.
7. Secondary Olefine Acids.
8. Etheric Secondary Olefine Acids.

1st. *Normal Acids*.—A normal acid of the lactic series may be defined as one in which an atom of carbon is united with oxatyl, hydroxyl, and at least one atom of hydrogen. The general formula of these acids is therefore



In this formula $\overset{+}{R}$ may be either hydrogen or any monad positive organic radical. The number of acids possessing the same atomic weight, and belonging to this division, is determined by the number of isomeric modifications of which the positive organic radical is susceptible. Thus, of the acids containing two, three, or four atoms of carbon, there can be only one of each belonging to this division, because these acids cannot contain a positive organic radical higher in the series than ethyl, and this radical is not susceptible of isomeric modification; but a normal acid containing propyl can have one isomer in this division, the two acids containing respectively propyl (CEtH_2) and isopropyl (CMe_2H). For acids of this division containing normal positive organic radicals only, the following general graphic formula may be given:—



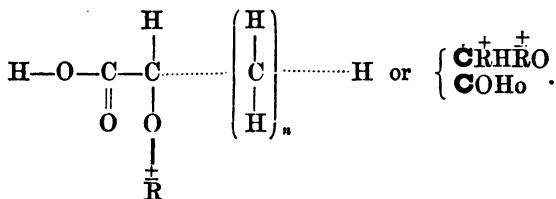
In the case of glycollic acid $n=0$.

The following are the acids at present known belonging to this division:—

| | |
|------------------------|--|
| Glycollic acid | $\left\{ \begin{array}{l} \text{CH}_2\text{Ho} \\ \text{COHo} \end{array} \right.$ |
| Lactic acid | $\left\{ \begin{array}{l} \text{CMeHHo} \\ \text{COHo} \end{array} \right.$ |
| Oxybutyric acid | $\left\{ \begin{array}{l} \text{CEtHHo} \\ \text{COHo} \end{array} \right.$ |
| Valerolactic acid..... | $\left\{ \begin{array}{l} \text{CPrHHo} \\ \text{COHo} \end{array} \right.$ |
| Leucic acid | $\left\{ \begin{array}{l} \text{CBuHHo} \\ \text{COHo} \end{array} \right.$ |

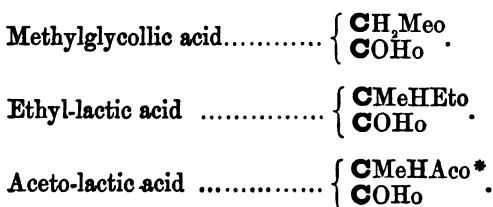
2nd. *Etheric Normal Acids*.—An etheric normal acid of the

lactic series is constituted like a normal acid, but contains a monad organic radical, positive or negative, in the place of the hydrogen of the *non-oxatylic* hydroxyl. The following is therefore the general formula of these acids: in the graphic formula n , as before, may = 0.



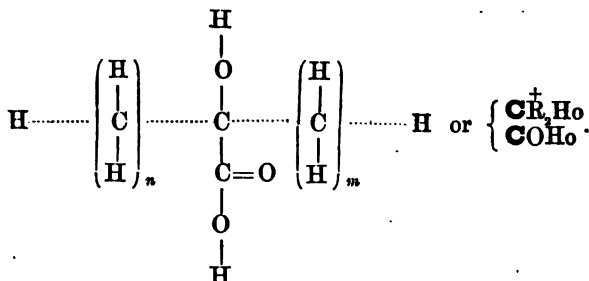
The number of possible isomers belonging to this division is very great; for, in addition to those of which the normal acids containing R^+ of the same value are susceptible, a host of others must result from the complementary variation of R^+ and R^- . The lowest member of the division, methylglycollic acid (isomeric with lactic acid), is the only one incapable of isomeric modification.

The following examples will serve to illustrate the constitution of the acids belonging to this division:—

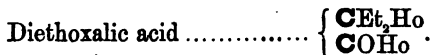
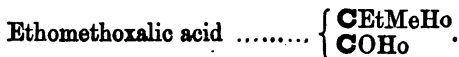
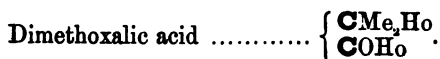


3rd. *Secondary Acids*.—A secondary acid of the lactic series is one in which an atom of carbon is united with oxatyl, hydroxyl, and *two semimolecules* of a monad positive organic radical. The general formula of these acids is:—

* Aco = peroxide of acetyl, $\text{C}_2\text{H}_3\text{O}_2$.

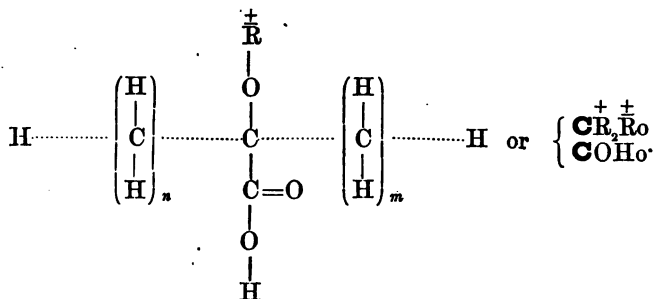


In the graphic expression, the values of n and m may differ; but both are positive integers, and neither may $=0$. In the symbolic formula $\overset{+}{\text{R}}$ must be a monad positive organic radical. The following examples will serve to illustrate their constitution:—

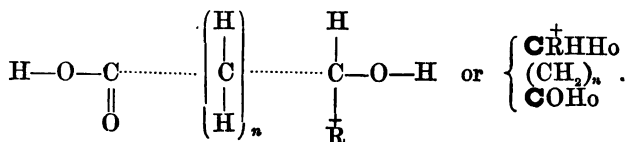


The number of acids possessing the same atomic weight, and belonging to this division, is determined, first, by the complementary variation of the two positive radicals, and, secondly, by the number of possible isomers of these radicals. The lowest two terms of the series are alone incapable of isomeric modification by either of the causes mentioned.

4th. *Etheric Secondary Acids*.—These acids stand in the same relation to the secondary as the etheric normal to the normal acids; they consequently contain a monad organic radical in the place of the hydrogen of the non-oxalylic hydroxyl. The following is therefore the general formula of these acids:—

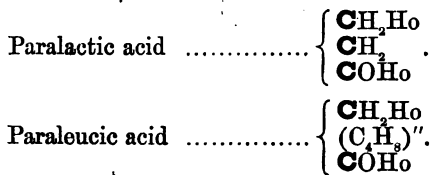


5th. *Normal Olefine Acids*.—A normal olefine acid belonging to the lactic series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is combined with not less than one atom of hydrogen. The following are the general graphic and symbolic formulæ of the acids belonging to this division :—



In both these formulæ n must be a positive integer and cannot =0, but R may be either hydrogen or a monad positive organic radical. The olefines of these acids may belong either to the ethylene or ethylidene series.

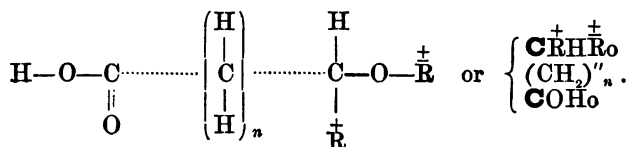
The following are the only acids at present known belonging to this division :—



The number of isomers in this division will obviously depend,

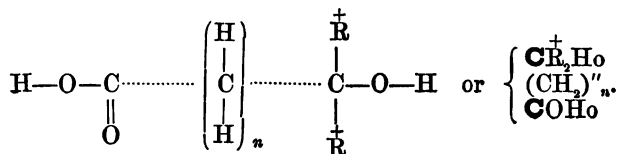
first, upon the complementary variations of $\overset{+}{R}$ and $(CH_2)_n$; secondly, upon the isomeric modifications of which $\overset{+}{R}$ is susceptible; and thirdly, upon the isomeric modifications of $(CH_2)_n$.

6th. *Etheric Normal Olefine Acids*.—These acids only differ from the normal olefine acids in having the hydrogen of the non-oxatylic hydroxyl replaced by an organic monad radical, positive or negative; their general formula is therefore,



As in the fifth division, n must be a positive integer and cannot $=0$, whilst $\overset{+}{R}$ may be either hydrogen or a monad positive organic radical; but $\overset{+}{R}$ must be a monad organic radical, either positive or negative.

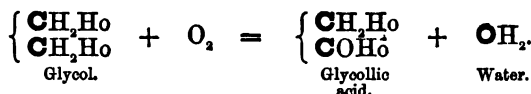
7th. *Secondary Olefine Acids*.—A secondary olefine acid of this series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is also combined with two monad positive organic radicals, as shown in the following formulæ:—



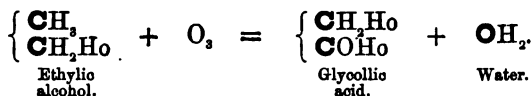
In both of these formulæ n must be a positive integer and cannot $=0$, and $\overset{+}{R}$ must be a monad positive radical.

8th. *Etheric Secondary Olefine Acids*.—These acids are related to the secondary olefine acids in the same way as the sixth division to the fifth. No member of the seventh or eighth division has yet been formed.

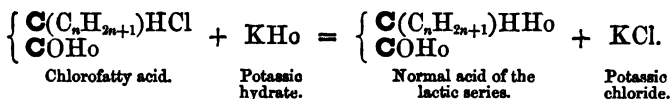
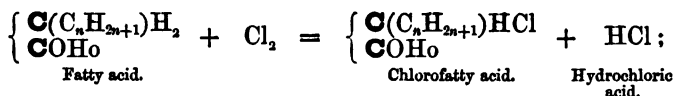
Formation of the Normal Acids.—1. By the oxidation of the glycols, or dihydric alcohols.



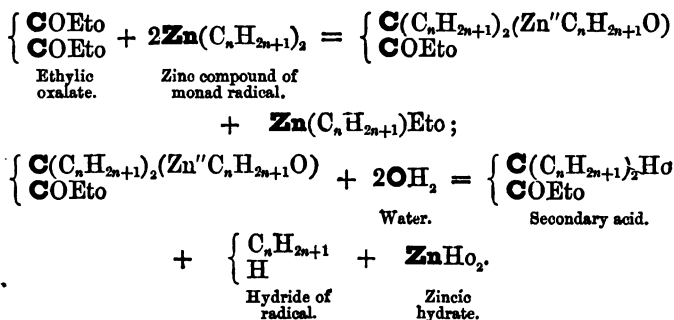
2. By the oxidation of the $\text{C}_n\text{H}_{2n+1}\text{Ho}$ alcohols:—



3. From the fatty acids, by converting them first into chloro-substitution acids, and then acting upon these compounds with potassic hydrate:—

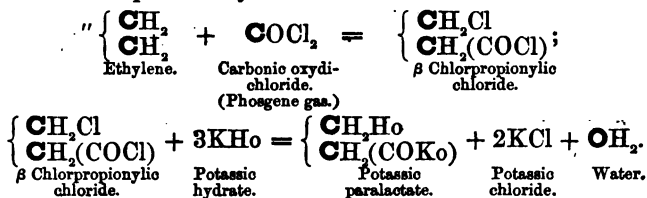


Formation of Secondary Acids.—By the action of the zinc compounds of the monad positive organic radicals upon ethylic oxalate, and the subsequent addition of water:—



Formation of Olefine Acids.—By uniting a dyad positive organic radical with carbonic oxydichloride (*phosgene gas*) under

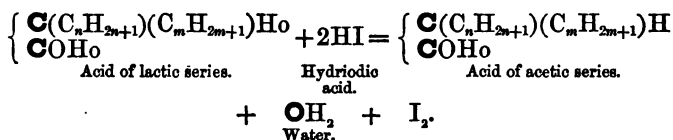
the influence of sunlight, and subsequently acting upon the product with potassic hydrate:—



Relations of the Lactic to the Acetic Series of Acids.

1. The transformation of the acetic or fatty into the normal lactic series of acids has been mentioned above (p. 141).

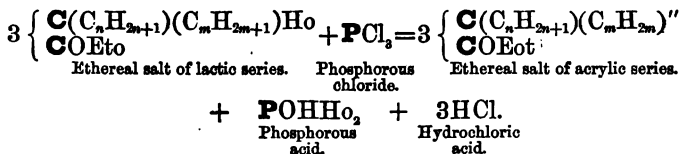
2. The converse operation is effected with the normal and secondary acids of the lactic series by means of hydriodic acid:—



If m does not = 0, the fatty acid will be a secondary one, like the member of the lactic series from which it is derived.

Relations of the Lactic to the Acrylic Series of Acids.

If the ethereal salts of the secondary acids of the lactic series be treated with phosphorous chloride, phosphoric chloride, phosphoric oxychloride, or phosphoric anhydride, the ethereal salts of the secondary acids of the acrylic series are produced:—



This reaction has not yet been accomplished with the normal acids of the lactic series.

A secondary lactic acid *minus* $\text{OH}_2 =$ an acrylic acid. The reverse of this operation has not been performed.

LACTIC ACID.



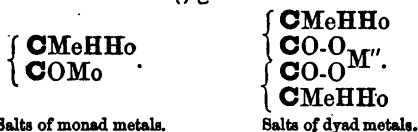
Sp. gr. of liquid 1.215.

Occurrence.—In sour milk, *Sauerkraut*, fluids of muscular tissue, gastric juice, saliva of diabetic patients. In the acid liquor of starch-factories, in blood, urine, tears, bile, &c. It is also a general product of putrefactive fermentation. The acid contained in animal fluids is *paralactic acid* (see p. 145).

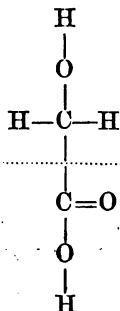
Preparation.—By fermenting sugar with putrid cheese.

For other processes, see pages 147 and 148.

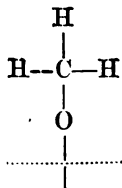
Its salts have the following general formulæ:—

*Isomerism in the Lactic Series.*

The synthetical study of the acids of this series affords an insight into numerous and interesting cases of isomerism. Commencing with the lowest member of the series, we have for glycollic acid the formula

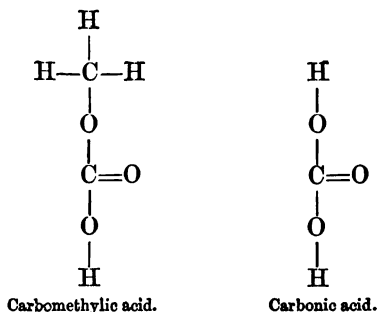


An inspection of this formula shows that glycollic acid admits of no isomeric modification, except with a total change of type. The part of the formula below the dotted line represents oxatyl, which cannot be altered without sacrificing the acid character of the compound; there remains therefore only the part of the formula above the dotted line, which admits of the following modification:—



The acid represented by the formula so modified no longer comes within the definition of the lactic series. It is carbomethylic acid, and differs essentially from glycollic acid and the lactic series in general, inasmuch as the carbon of its negative radical, oxatyl, is linked to the carbon of the positive radical by oxygen*.

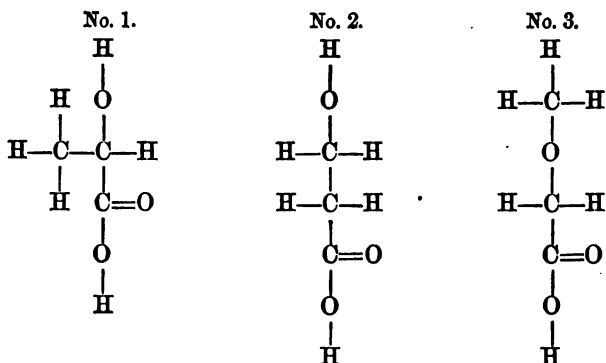
* Bearing this constitution of carbomethylic acid in mind, we have only to go one step further in order to perceive the constitution of carbonic acid itself, and the explanation of the anomalous basicity of this acid; for if, in the above graphic formula for carbomethylic acid, we replace the methyl by hydrogen, we have:—



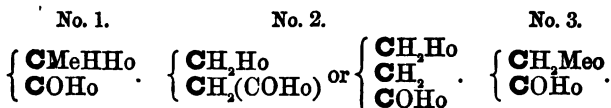
It is thus evident that the radical oxatyl, when united with hydroxyl, has sufficient negative power to produce a feebly dibasic acid; but inasmuch as

There being no decisive evidence that *homolactic acid* differs from glycollic acid, experiment and theory both agree in asserting that the formula $C_2H_4O_3$ represents only one acid in the lactic series.

Proceeding now one step higher in this series, we have in the formula of lactic acid an expression capable of the following three variations without quitting the lactic type:—



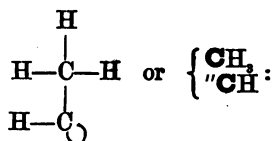
Or, expressed symbolically:—



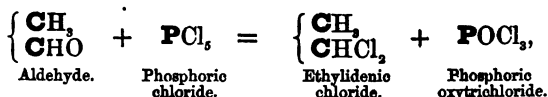
All the acids represented by the above formulæ are known. The first expresses the constitution of lactic acid, which belongs to the normal division $\left(\left\{ \begin{array}{l} \text{CR}^+\text{HHo} \\ \text{COHo} \end{array} \right\} \right)$ of the series, described at page 135; the second shows the atomic arrangement of paralactic acid; whilst the third represents methylglycollic acid. The proof that the first two of these acids are so constituted is afforded by the synthetic processes sometimes

carbonic acid is not included in the category of organic acids, it forms no exception to the law that an organic acid containing n semimolecules of oxatyl is n -basic.

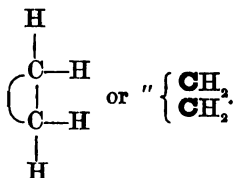
employed to produce them; for ethylenic cyanhydrate is converted by ebullition with potash into a salt of lactic acid, whilst ethylenic cyanhydrate is transformed under similar circumstances into paralactic acid. It has also been mentioned above, that paralactic acid is produced by the action of phosgene gas upon ethylene. Now the formation of ethylidene, or rather of its compounds, scarcely leaves a doubt that this body, if isolated, would have the following atomic constitution:—



it would consist of a semimolecule of methyl and an atom of hydrogen, both united with an atom of carbon two of the bonds of which satisfy each other. Thus the formation of ethylidene chloride from aldehyde and phosphoric chloride takes place as follows:—

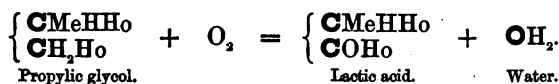


the oxygen in the aldehyde being simply replaced by chlorine. There now only remains one possible formula for ethylene, viz.

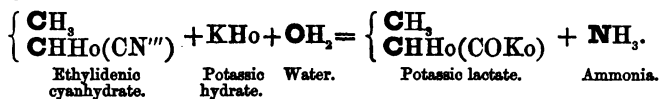


Such, then, being the constitution of ethylidene and ethylene, it follows that the former ought to give rise to an acid of the constitution shown in formula No. 1, whilst ethylene should produce an acid agreeing with formula No. 2. The acids actually produced from these sources are lactic and paralactic

acids; hence No. 1 is the constitutional formula of lactic acid, and No. 2 that of paralactic acid—a conclusion which harmonizes perfectly with all the reactions in which the production of these acids can be traced. Thus in the formation of lactic acid by the oxidation of propylic glycol, we have



Again, in the production of this acid from ethylenic cyanhydrate,



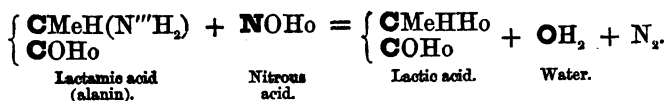
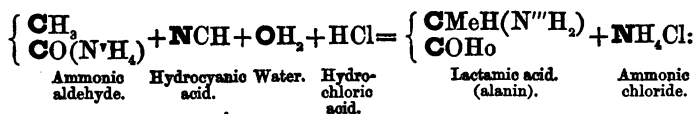
The formula given for potassic lactate in this equation is only apparently different in type from that previously used for lactic acid, since



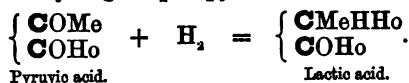
In the reaction by which chloropropionic acid is transformed into lactic acid we have the following change:—



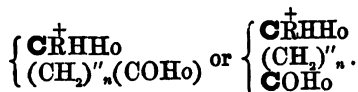
The production of lactamic acid (*alanin*), and that of lactic acid from the latter by the action of nitrous acid, are also clearly confirmatory of the above view.



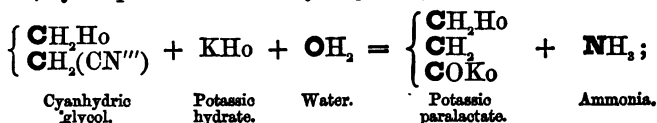
Not the least interesting reaction illustrative of the constitution of lactic acid is the formation of this acid by the action of nascent hydrogen upon pyruvic acid:—



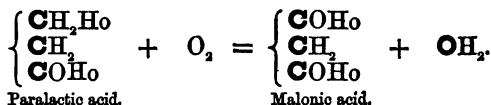
In a similar manner it can be demonstrated that the above formula No. 2 expresses the constitution of paralactic acid, which belongs to the fifth or olefine division of these acids,



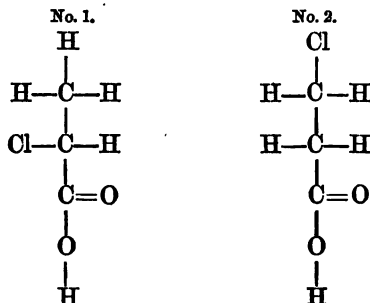
That paralactic acid possesses this constitution is proved, first, by its production from cyanhydric glycol—



secondly, by its formation from phosgene gas and ethylene (see p. 142); and thirdly, by its conversion into malonic acid by the oxidizing action of dipotassic dichromate:—

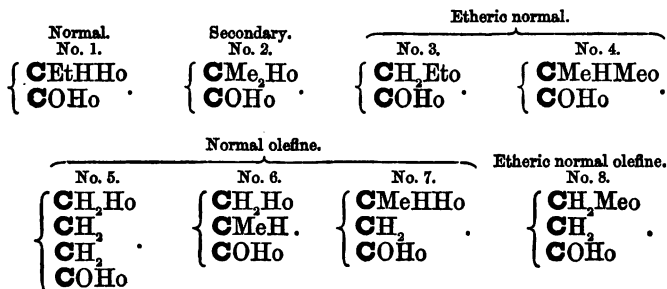


By the action of water upon the chloride of β chlorpropionyl, a body of the composition of chloropropionic acid is obtained; but inasmuch as this body yields paralactic acid by ebullition with potash, whilst chloropropionic acid gives under the same circumstances lactic acid, it follows that the former chloro-acid must be isomeric, and not identical, with the latter. Now, although the formula of propionic acid does not admit of any isomer, yet that of chloropropionic acid does, as is seen in the following graphic formulæ:—



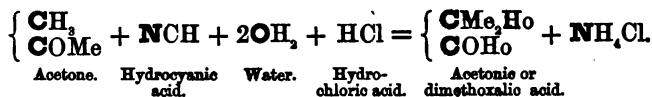
A comparison of these formulæ with those of lactic and paralactic acids (p. 145) shows at a glance that No. 1 is the chloropropionic acid which yields lactic acid, whilst No. 2 is iso-chloropropionic acid, which, by the substitution of its chlorine by hydroxyl, must yield paralactic acid. By the action of nascent hydrogen, both isomeric chlorides will obviously produce the same propionic acid.

The cause of the isomerism of methyl-glycollic acid (No. 3, p. 145) is so obvious as to require no further explanation. Proceeding to the next higher stage in the series, such is the rapid increase of isomeric forms, that we now encounter no less than eight possible isomers, all within the lactic family.



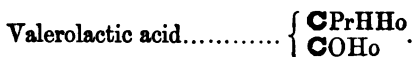
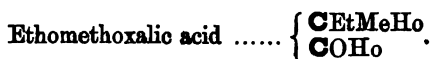
Of these acids, Nos. 1, 2, and 3 are known. No. 1 is oxy-butyric acid; No. 2 is dimethoxalic acid, which is identical with acetic acid. This being the case, the formation of the

latter by the action of hydrocyanic and hydrochloric acids upon acetone is easily intelligible:—

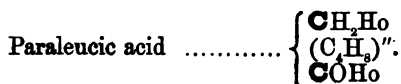
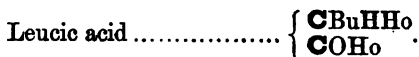


The third of the above formulæ is that of ethyl-glycollic acid.

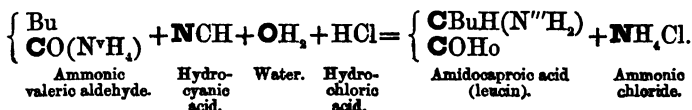
Of the possible acids containing five atoms of carbon, only two, viz. ethomethoxalic acid and valerolactic acid, are known. The cause of the isomerism of these two acids is seen at once from an inspection of their constitutional formulæ:—



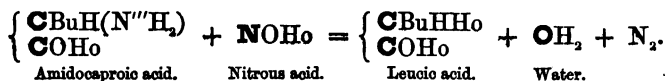
Of acids containing six atoms of carbon, the following three are known:—



The above formula for leucic acid is founded upon a reaction for the synthetical production of amidocaproic acid from valeric aldehyde and hydrocyanic acid. Valeric acid contains butyl; consequently valeric aldehyde has the constitution expressed by the formula $\left\{ \begin{array}{l} \text{Bu} \\ \text{COH} \end{array} \right\}$; and the reaction in question is therefore explained by the following equation:—



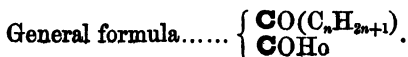
Such being the rational formula of amidocaproic acid, its transformation into leucic acid by nitrous acid determines the constitution of leucic acid :—



CHAPTER XIX.

THE ACIDS.

4. PYRUVIC SERIES.



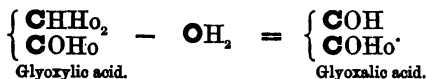
In this formula n may = 0.

The following list contains all the known members of this series :—

| | | |
|--------------------------|---|----------------|
| Pyruvic acid | $\left\{ \begin{array}{l} \text{COMe} \\ \text{COH}_o \end{array} \right\}.$ | Boils at 165°. |
| Convolvulinoleic acid... | $\left\{ \begin{array}{l} \text{CO(C}_{11}\text{H}_{23}) \\ \text{COH}_o \end{array} \right\}.$ | Fuses at 42°. |
| Jalapinoleic acid..... | $\left\{ \begin{array}{l} \text{CO(C}_{14}\text{H}_{29}) \\ \text{COH}_o \end{array} \right\}.$ | „ 65°. |
| Ricinoleic acid | $\left\{ \begin{array}{l} \text{CO(C}_{18}\text{H}_{33}) \\ \text{COH}_o \end{array} \right\}.$ | „ 0°. |

Pyruvic acid only is well known.

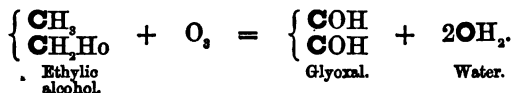
The first member of this series would have the formula $\left\{ \begin{array}{l} \text{COH} \\ \text{COH}_o \end{array} \right\}.$ This acid is believed to be formed by the dehydration of glyoxylic acid; but its existence has not yet been satisfactorily demonstrated :—



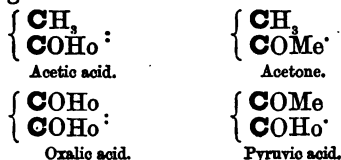
The aldehyde of this acid, however, is known. It is called glyoxal, and its formula is:—



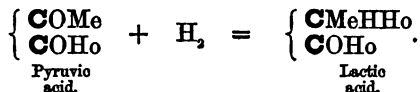
Glyoxal is produced by the oxidation of ethylic alcohol by nitric acid:—



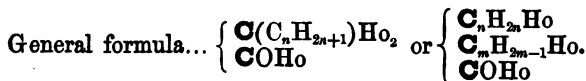
These acids are the semi-ketones of oxalic acid, and they stand in much the same relation to this acid as that which acetone occupies with regard to acetic acid:—



The pyruvic series is also closely related to the lactic series; pyruvic acid absorbs hydrogen and is converted into normal lactic acid:—

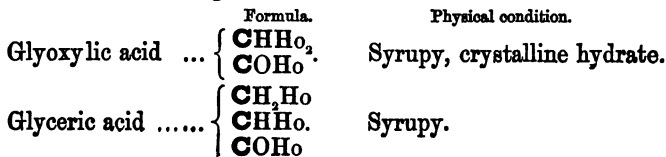


5. THE GLYOXYLIC SERIES OF ACIDS.



In the second formula n may = 0.

The two following acids of this series are known:—



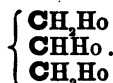
These acids are trihydric, but monobasic, and are related to the glycerin series of alcohols in the same way that the members of the lactic series are related to the glycols:—



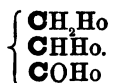
Glycol.



Glycollic acid.

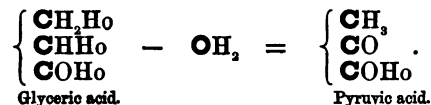


Glycerin.



Glyceric acid.

By a reaction similar to that which is believed to produce glyoxalic acid from glyoxylic acid, glyceric acid yields pyruvic acid:—



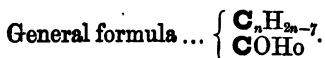
Glyceric acid.

Pyruvic acid.

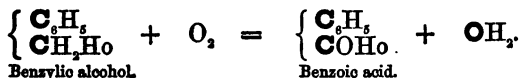
CHAPTER XX.

THE ACIDS.

6. THE BENZOIC OR AROMATIC SERIES OF ACIDS.



Formation.—1. By the oxidation of the aromatic or $\text{C}_n\text{H}_{2n-7}\text{Ho}$ alcohols:—

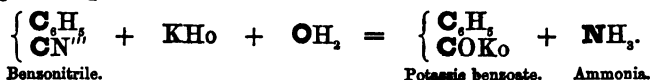


Benzyl alcohol.

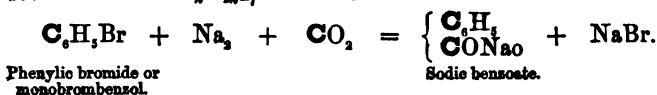
Benzoic acid.

2. By the oxidation of the aromatic aldehydes. Thus benzoic acid is formed from benzoic aldehyde, or oil of bitter almonds (see p. 112).

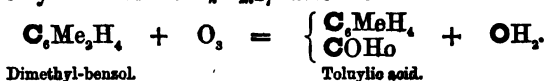
3. By the action of alkalies on the nitriles or abnormal cyanides. Thus potassic benzoate is formed by the action of potash upon Benzonitrile:—



4. By the action of sodium and carbonic anhydride on the bromides of the $\text{C}_n\text{H}_{2n-7}$ radicals:—



5. Some members of the series are produced by the oxidation of the hydrides of the $\text{C}_n\text{H}_{2n-7}$ radicals:—

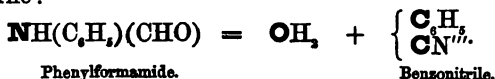


6. The acids of the aromatic series may be obtained from the monamines of the series containing one atom less of carbon.

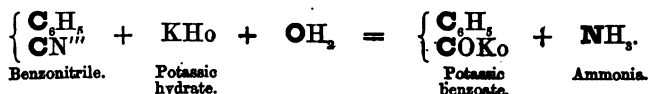
Thus Phenylamine, when distilled with oxalic acid, produces phenylformamide:—



Phenylformamide, by the action of heat, gives water and benzonitrile:—



Benzonitrile, heated with potassic hydrate, gives potassic benzoate and ammonia:—



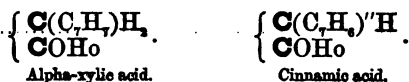
Toluylic acid, $\left\{ \begin{array}{l} \text{C}_6\text{H}_4\text{Me} \\ \text{COH}_2 \end{array} \right.$, can thus be obtained from toluidine, $\text{NH}_2(\text{C}_6\text{H}_4\text{Me})$.

The following terms of this series are known :—

| | | Melting-point. | Boiling-point. |
|--------------------------|---|--|---|
| Phenoic acid | $\left. \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{COH}_o \end{array} \right\} \dots$ | 60°. | — |
| Collinic acid | | 97°. | — |
| Benzenic acid | | above...110°. | 235°. |
| Benzoic acid | $\left\{ \begin{array}{l} \text{C}_6\text{H}_5 \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | 121°·4. | 239°. |
| Toluylic acid | $\left\{ \begin{array}{l} \text{C}_6\text{MeH}_4 \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | 175°·0. | — |
| Alpha-toluylic acid..... | $\left\{ \begin{array}{l} \text{C}_6\text{PhH}_2 \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | 76°·5. | 265°·5. |
| Xylic acid | $\left\{ \begin{array}{l} \text{C}_6\text{Me}_2\text{H}_2 \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | $\left\{ \begin{array}{l} 103°·0. \\ 126°·0. \\ 163°·0. \end{array} \right.$ | $\left\{ \begin{array}{l} 273° \\ \text{—} \\ \text{—} \end{array} \right.$ |
| Alpha-xylic acid | $\left\{ \begin{array}{l} \text{C}(\text{C}_6\text{MeH}_4)_2 \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | 42°·0. | — |
| Cuminic acid | $\left\{ \begin{array}{l} \text{C}_9\text{H}_{11} \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | 92°·0. | — |
| Alpha-cymic acid | $\left\{ \begin{array}{l} \text{C}_9\text{Et}_2\text{H}_2 \\ \text{COH}_o \end{array} \right. \dots\dots\dots$ | — | — |

These acids have the same constitution as those of the acetic series, but contain the $\text{C}_n\text{H}_{2n-7}$ radicals.

They have been much less studied than the acetic series ; and further investigation will probably bring to light other series holding towards them the same relation as the acrylic, glycollic, pyruvic, and glyoxylic series bear to the acetic series. Already an acryloid acid of this section is known corresponding to alpha-xylic acid :—



Cinnamic acid is decomposed, like the acids of the acrylic series, when heated with fused potassic hydrate ; it gives, under these circumstances, potassic acetate and benzoate. For the analogous reaction in the acrylic series see p. 132.

Atropic acid, obtained by the action of alkalis on atropine, has the formula $\left\{ \begin{array}{l} \text{C}_9\text{H}_7 \\ \text{COH}_o \end{array} \right.$ and is isomeric with cinnamic acid.

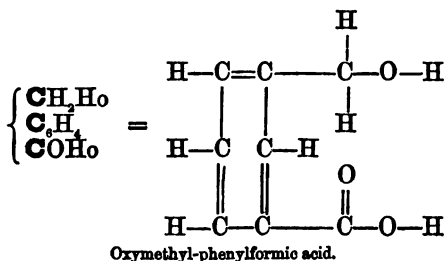
Salicylic acid (with which oxybenzoic acid and parabenzoic acid are isomeric) is the lactic acid of benzoic acid :—



and the oil of meadow-sweet (*Spiræa ulmaria*) is generally regarded as the aldehyde of salicylic acid :—



Oxymethyl-phenylformic acid is the lactic representative of tolylic acid, from which last-named acid it is prepared. Its constitution will be understood from the following graphic formula :—



The following acids also probably belong to the phenyl-lactic series :—

| Isomeric. | | | | Melting-point. |
|-----------|--------------------------|---|-------|----------------|
| | | | | |
| { | Cresotic acid | $\left\{ \begin{array}{l} \text{C}_7\text{H}_7\text{O} \\ \text{COH}_o \end{array} \right.$ | 153°. | |
| | Anisic acid | $\left\{ \begin{array}{l} \text{C}_8\text{H}_7\text{Meo} \\ \text{COH}_o \end{array} \right.$ | 175°. | |
| | Paraphloretic acid | $\left\{ \begin{array}{l} \text{C}_8\text{H}_7\text{Meo} \\ \text{COH}_o \end{array} \right.$ | — | |
| | Thymotic acid | $\left\{ \begin{array}{l} \text{C}_{10}\text{H}_{13}\text{O} \\ \text{COH}_o \end{array} \right.$ | 120°. | |

BENZOIC ACID.



Molecular weight = 122. *Molecular volume* $\square\square$. 1 litre of benzoic acid vapour weighs 61 criths. *Fuses* at $121^{\circ}4$. *Boils* at 239° .

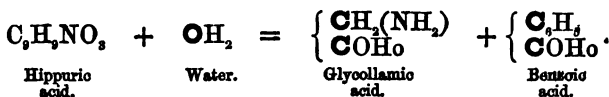
Occurrence.—In many balsams and gums. In putrid urine.

Preparation.—1. By the oxidation of oil of bitter almonds (p. 112).

2. By the action of fused potassic hydrate on cinnamic acid :—



3. By boiling hippuric acid with hydrochloric acid :—



4. By the action of oxidizing agents on casein or gelatin.

5. From gum benzoin, by sublimation, or by extraction with potassic hydrate and subsequent precipitation of the acid by hydrochloric acid.

6. Styrol treated with a solution of potassic permanganate gives benzoic acid and carbonic anhydride :—



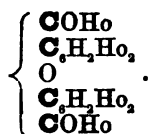
Gallic acid is a tetrahydric monobasic acid of the formula



It may therefore be regarded as benzoic acid in which three

atoms of hydrogen have been replaced by three semimolecules of hydroxyl.

Tannic acid is obtained by the abstraction of one molecule of water from two molecules of gallic acid. Its constitutional formula is:—



CHAPTER XXI.

THE ACIDS.

DIBASIC ACIDS.

General formula... $\text{A}(\text{COH}_o)_2$ or $\left\{ \begin{array}{c} \text{A}(\text{COH}_o) \\ \text{B}(\text{COH}_o) \end{array} \right\}$,

A and B being dyad radicals containing $\text{C}_n\text{H}_m\text{O}_r$.

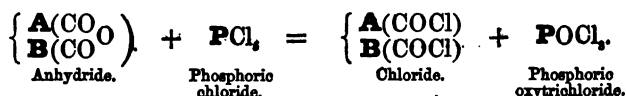
These acids all contain two semimolecules of oxatyl; and if in the general formula n , m , and $l = 0$, oxalic acid will be the first term of the series.

Formation.—Many of the dibasic acids are produced by the oxidation of substances, the molecules of which are richer in carbon, such as oils and fats. Others are found ready formed in nature.

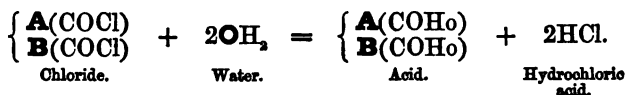
Reactions.—1. By the action of dehydrating substances, and even sometimes by heat alone, these acids lose water, forming anhydrides:—



2. If the anhydride be submitted to the action of phosphoric chloride, an atom of oxygen is replaced by two of chlorine:—



3. Both the anhydrides and the chlorides are reconverted into the acids by the action of water:—



The dibasic acids may be divided into the four following series:—

$$1. \text{ Succinic or acetoid series } \dots\dots\dots \left\{ \begin{array}{l} \text{C}_n\text{H}_{2n}(\text{COHo}) \\ \text{C}_m\text{H}_{2m}(\text{COHo}) \end{array} \right\}.$$

In the first member of the series $m = 0$.

$$2. \text{ Fumaric or acryloid series } \dots\dots\dots \left\{ \begin{array}{l} \text{C}_n\text{H}_{2n-1}(\text{COHo}) \\ \text{C}_n\text{H}_{2n-1}(\text{COHo}) \end{array} \right\}.$$

$$3. \text{ Malic or lactoid series } \dots\dots\dots \left\{ \begin{array}{l} \text{C}_n\text{H}_{2n-1}\text{Ho}(\text{COHo}) \\ \text{C}_n\text{H}_{2n}(\text{COHo}) \end{array} \right\}.$$

$$4. \text{ Tartaric or glyoxyloid series } \dots\dots\dots \left\{ \begin{array}{l} \text{C}_n\text{H}_{2n-1}\text{Ho}(\text{COHo}) \\ \text{C}_n\text{H}_{2n-1}\text{Ho}(\text{COHo}) \end{array} \right\}.$$

The first and second series are dibasic and *dihydric*; the third, dibasic and *trihydric*; and the fourth, dibasic and *tetrahydric*.

1. THE SUCCINIC OR ACETOID SERIES.

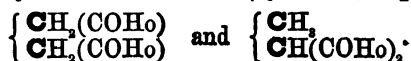
$$\text{General formula } \dots \left\{ \begin{array}{l} \text{COHo} \\ \text{C}_n\text{H}_{2n} \\ \text{C}_n\text{H}_{2n} \\ \text{COHo} \end{array} \right\} \text{ or } \left\{ \begin{array}{l} \text{COHo} \\ \text{C}_n\text{H}_{2n} \\ \text{COHo} \end{array} \right\}.$$

In addition to oxalic acid (oxetyl) which many chemists

regard as the first member of this series, the following are known:—

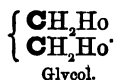
| | | |
|------------------------|--|-------------------------------|
| Malonic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{CH}_2 \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 140°. |
| Succinic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{CH}_2 \\ \text{CH}_2 \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 180°. Boils at 235°. |
| Isosuccinic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{CMeH} \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 130°. |
| Pyrotartaric acid ... | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_2\text{H}_3 \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 112°. Boils at 200°. |
| Adipic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_4\text{H}_8 \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 140°. |
| Pimelic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_5\text{H}_{10} \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 134°. |
| Suberic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_6\text{H}_{12} \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 125°. |
| Anchoic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_7\text{H}_{14} \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 116°. |
| Sebacic acid..... | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_8\text{H}_{16} \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 127°. |
| Roccellic acid | $\begin{Bmatrix} \text{COH}_o \\ \text{C}_{10}\text{H}_{20} \\ \text{COH}_o \end{Bmatrix}$ | Fuses at 132°. Boils at 200°. |

It is obvious that there may be several modifications of each of these acids. Thus there are two succinic acids, one containing ethylene, and the other ethylidene (see p. 168):—

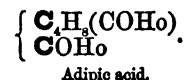
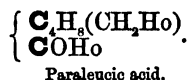
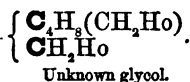
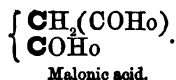
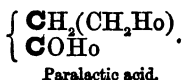
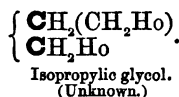


1. *Relations of the Succinic to the Lactic Series of Acids and to the Glycols.*

These acids are related to the lactic series and to the glycols in the same way as the fatty acids are related to the monacid alcohols:—

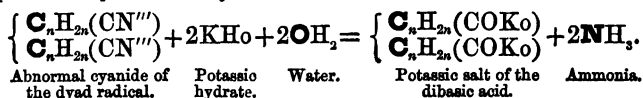


This relation, however, does not strictly extend beyond the first member, although it may be partially traced in the relations of malonic and adipic acid to paralactic and paraleucic acid:—

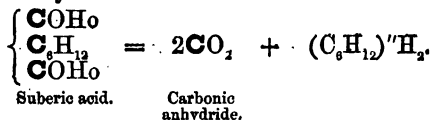


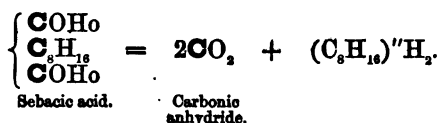
2. *Relations of the Succinic Series to the Dyad Radicals.*

1. The acids of the succinic series are intimately related to the dyad radicals, the nitriles or abnormal cyanides of which are readily converted into dibasic acids by ebullition with potassic hydrate or hydrochloric acid:—



2. Some of these acids, when heated with excess of caustic baryta, give up two atoms of carbonic anhydride, yielding the hydrides of the dyad radicals:—

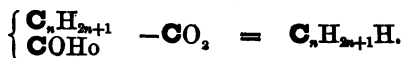




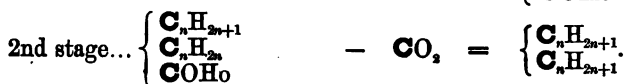
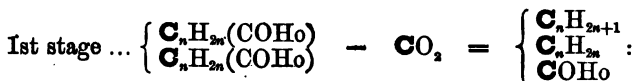
These reactions are the analogues, in the dyad series, of the process by which marsh-gas is obtained from acetic acid. The hydrides of the dyad radicals so obtained are isomeric with those of the corresponding monad radicals.

The elimination of carbonic anhydride from a monobasic acid can only take place once, while from a dibasic acid it takes place in two successive stages:—

In the case of a monobasic acid,

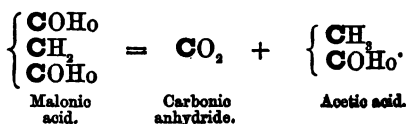
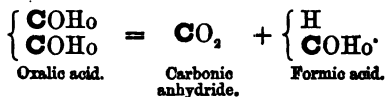


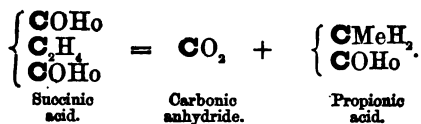
In the case of a dibasic acid,



3. Relations of the Succinic to the Acetic Series of Acids.

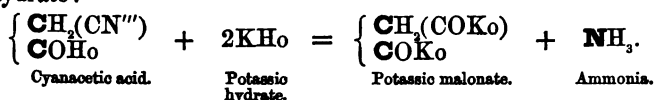
1. By the loss of the elements of carbonic anhydride, the first three members of the succinic series are converted into members of the acetic series, containing one atom of carbon less:—





In the first two cases the action of heat alone is sufficient to effect the transformation; but in the third the affinity of lime for carbonic anhydride must be superadded.

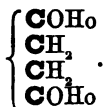
2. Conversely, the members of the acetic series may be converted into those of the succinic containing one atom of carbon more, by replacing one atom of the hydrogen in the positive radical of the acid by cyanogen, and then boiling with potassic hydrate:—



The conversion of formic acid into oxalic acid, by heating with potassic hydrate, also belongs to this class of reactions:—



SUCCINIC ACID.

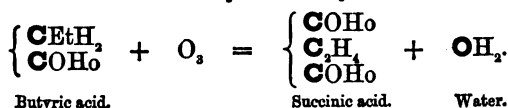


Fuses at 180°. Boils at 235°. Dissolves in 20 parts of cold water.

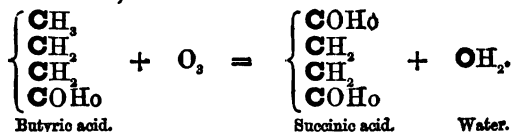
Occurrence.—In amber; in some kinds of lignite; in the resin of some kinds of pine; also in many other vegetable and animal substances.

Formation.—1. By the action of potassic hydrate upon abnormal ethylenic cyanide (p. 161): this reaction proves that succinic acid contains ethylene, and that its constitutional formula is as given above.

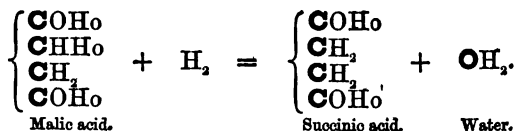
2. By the oxidation of butyric acid by nitric acid :—



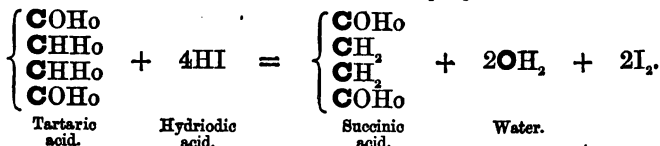
The nature of this reaction is more clearly seen with fully developed formulæ, thus :—



3. By the reduction of malic acid by fermentation, or by hydriodic acid :—

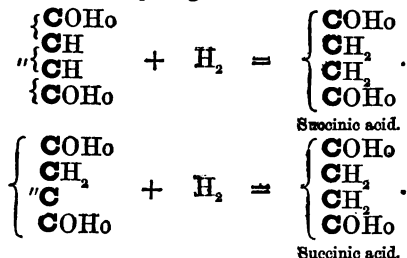


4. By the reduction of tartaric acid by hydriodic acid :—

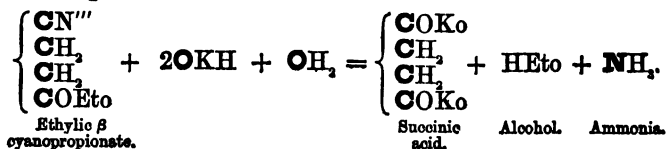


It is evident that this reaction is perfectly analogous to that by which lactic acid is transformed into propionic acid (p. 125).

5. The two isomeric acids, fumaric and maleic acids, are converted by nascent hydrogen into succinic acid :—

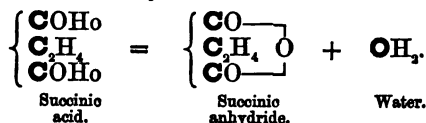


6. By boiling ethylic β cyanopropionate with solution of caustic potash :—

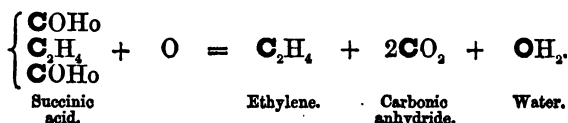


The two processes by which succinic acid is generally prepared are, the distillation of amber and the fermentation of calcic malate.

Reactions.—1. By distillation, succinic acid splits almost entirely into succinic anhydride and water :—

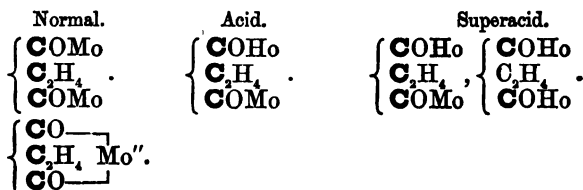


2. Under the action of nascent oxygen produced by electrolysis, succinic acid yields ethylene, carbonic anhydride, and water :—

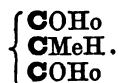


3. Succinic acid may be boiled for hours with concentrated nitric acid without suffering any change ; neither is it affected by a mixture of potassic chlorate and hydrochloric acid ; but it produces acetic acid when distilled with sulphuric acid and manganic oxide.

4. Succinic acid forms three kinds of salts, viz. :—

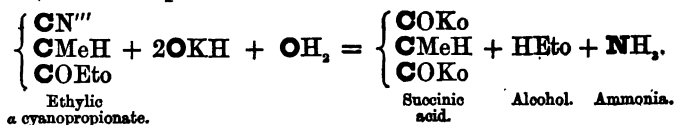


ISOSUCCINIC ACID.



Fuses at 130°. Dissolves in 5.4 parts of cold water.

Formation.—By boiling ethylic α cyanopropionate with solution of caustic potash:—



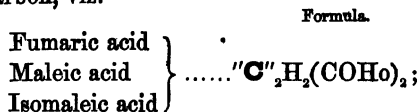
CHAPTER XXII.

THE ACIDS.

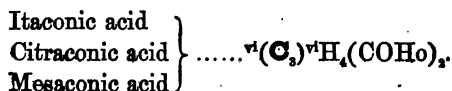
2. FUMARIC OR ACRYLOID SERIES.

General formula ... " $\begin{Bmatrix} \text{C}_n\text{H}_{2n-1}(\text{COHo}) \\ \text{C}_n\text{H}_{2n-1}(\text{COHo}) \end{Bmatrix}$ or $\text{C}_n\text{H}_{2n-2}(\text{COHo})_2$.

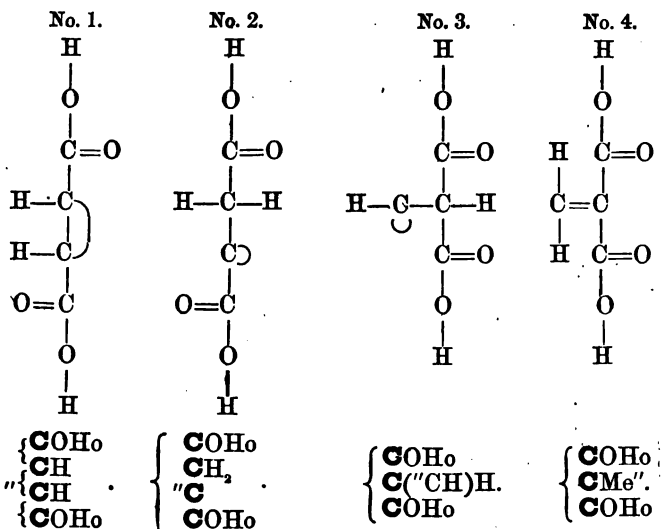
In this series there are three isomeric acids containing four atoms of carbon, viz.



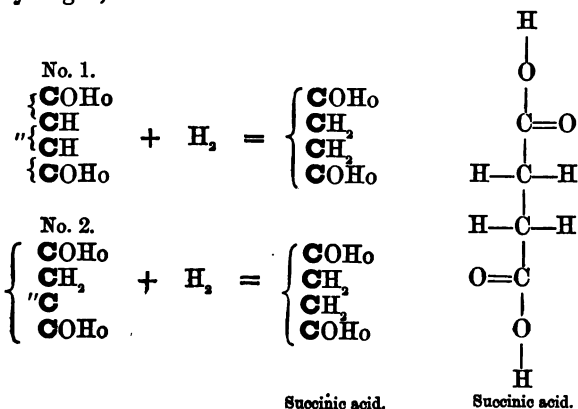
and three other isomeric acids containing five atoms of carbon, viz.



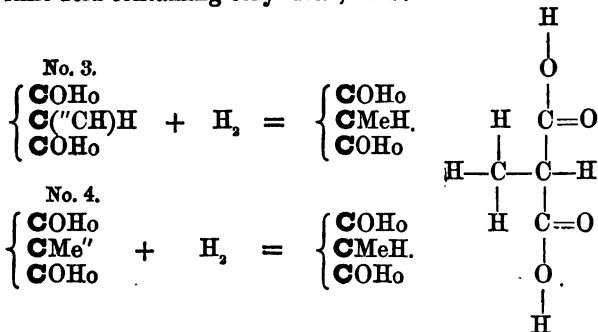
Constitutional notation predicts the existence of a fourth acid belonging to the four-carbon group. The following are the four possible formulæ for these acids:—



Of these formulæ, Nos. 1 and 2 represent fumaric and maleic acids. Data are still wanting to enable its own particular formula to be assigned to each of these acids; but the first two formulæ must belong to fumaric and maleic acids, because both these acids yield succinic acid under the influence of nascent hydrogen, thus:—



That succinic acid contains ethylene ($\left\{ \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \right\}$) and not ethylidene ($\left\{ \begin{smallmatrix} \text{CH}_3 \\ \text{CH} \end{smallmatrix} \right\}$), is proved by its formation from abnormal ethylenic cyanide (p. 161); but formulæ Nos. 3 and 4 give, by the addition of two atoms of hydrogen, the formula of isosuccinic acid containing ethylidene, thus:—

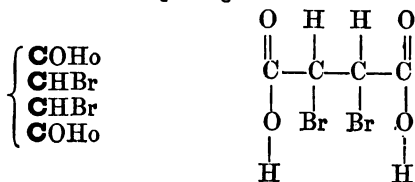


Isosuccinic acid.

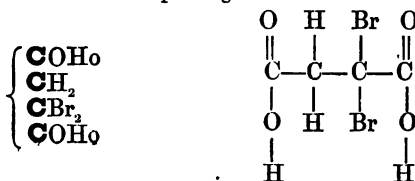
Isosuccinic acid.

Fumaric acid combines directly with bromine, producing dibromosuccinic acid. Maleic acid also combines directly with bromine, producing isodibromosuccinic acid. The following formulæ show the nature of this isomerism:—

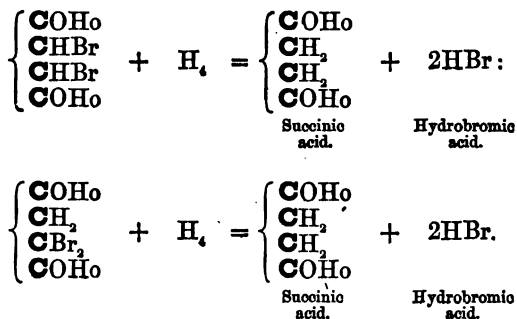
Corresponding to No. 1.



Corresponding to No. 2.



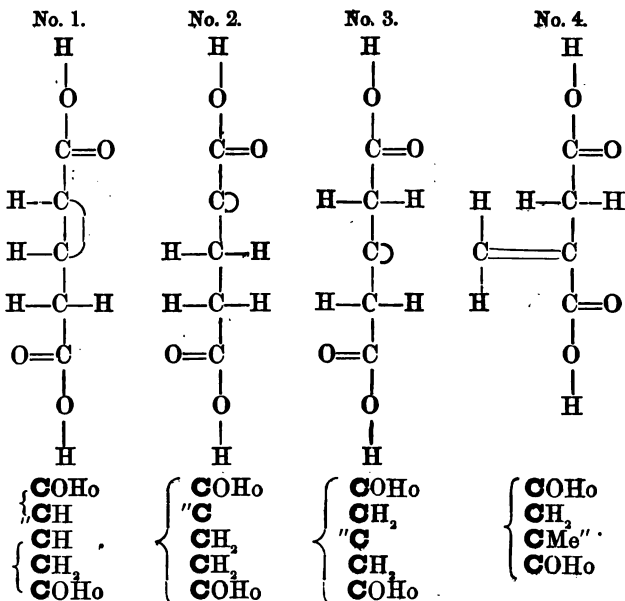
When acted upon by nascent hydrogen, both these isomeric bromo-acids produce, as might be expected, the same succinic acid:—



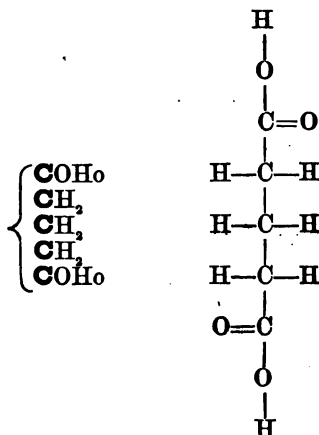
Inasmuch as formulæ Nos. 1 and 2 belong to fumaric and maleic acids, it follows that one of the two remaining constitutional formulæ must be that of isomaleic acid. It is impossible at present to determine which of these formulæ is to be assigned to this acid; but in any case there can scarcely be a doubt that isomaleic acid, when treated with nascent hydrogen, will yield isosuccinic acid, as shown above.

Of a similar character is the relation subsisting between the isomeric acids of this series containing five atoms of carbon, viz. itaconic acid, citraconic acid, and mesaconic acid. There are no less than ~~seven~~ possible formulæ for this five-carbon group of acids; but the three individual formulæ belonging to the three known acids cannot at present be determined. The following four formulæ will serve as specimens of the whole, and as illustrations of the cause of isomerism in these acids:—

fourteen

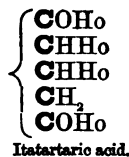
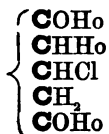
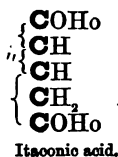


Itaconic, citraconic, and mesaconic acids stand in the same relation to pyrotartaric acid as fumaric and maleic acids occupy with regard to succinic acid; for, when submitted to the action of nascent hydrogen, they all yield the same pyrotartaric acid; and it is therefore highly probable that the first three of the above formulæ belong to these acids. The formula of pyrotartaric acid is

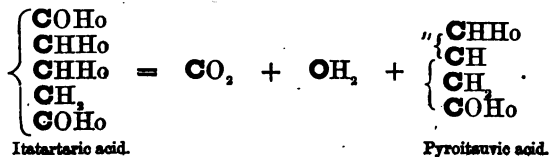


Treated with bromine, the three acids yield three isomeric brominated acids, which are transformed by nascent hydrogen into the same pyrotartaric acid.

By the action of hypochlorous acid on itaconic acid and subsequent replacement of the chlorine by hydroxyl, itatartaric acid is formed:—



Itatartaric acid, by distillation at 125°, gives carbonic anhydride, water, and pyroitaucic acid, which appears to belong both to the lactic and the acrylic series of acids.



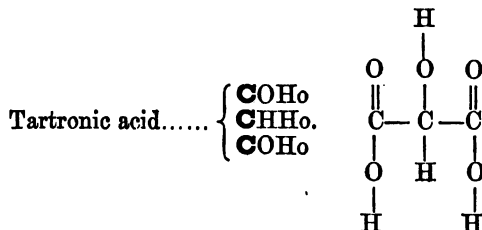
CHAPTER XXIII.

THE ACIDS.

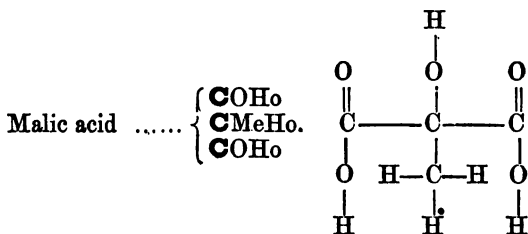
3. MALIC OR LACTOID SERIES.

General formula..... $\left\{ \begin{array}{l} \text{C}_n\text{H}_{2n-1}\text{Ho}(\text{COHo}) \\ \text{C}_n\text{H}_{2n}(\text{COHo}) \end{array} \right.$ or $\left\{ \begin{array}{l} \text{COHo} \\ \text{C}_n\text{H}_{2n-1}\text{Ho} \\ \text{COHo} \end{array} \right.$

Only two acids belonging to this series are known, viz. tartronic acid and malic acid. Like lactic acid, they both contain a semimolecule of *non-oxalylic* hydroxyl:—



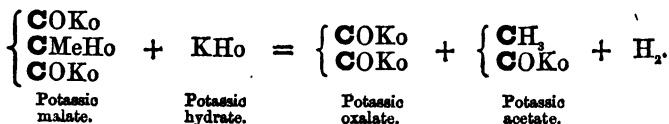
This acid may be regarded as the product of the oxidation of glycerin, although it has not yet been so produced. It is obtained by the gentle oxidation of tartaric acid (p. 175).



Malic acid may be viewed as the product of the oxidation of the hitherto undiscovered butyl glycerin, $\left\{ \begin{array}{l} \text{CH}_2\text{Ho} \\ \text{CMeHo} \\ \text{CH}_2\text{Ho} \end{array} \right.$

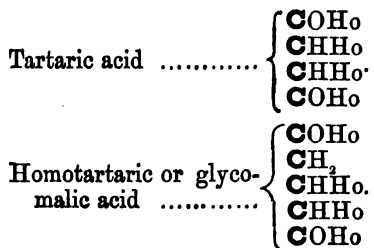
This acid is contained in apples, and in many other fruits.

When gently heated with potassic hydrate, hydrogen is evolved, potassic oxalate and acetate being produced:—

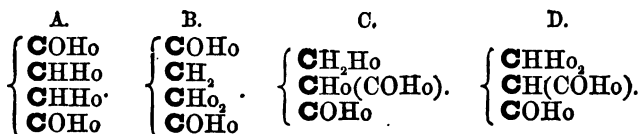


4. TARTARIC OR GLYOXYLOID SERIES.

This series contains at present only two members; but these have numerous isomers, which have been studied, however, only in the case of the first. Like the glyoxylic series, these acids contain two semimolecules of *non-oxalylic* hydroxyl.



There are four possible constitutional formulæ for tartaric acid, viz.:—



The known varieties of tartaric acid are also limited to four, viz.:—

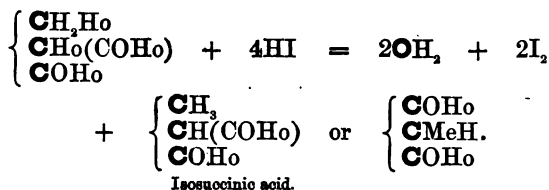
1. Dextrotartaric or common tartaric acid, so called from its property of causing the plane of polarization of a ray of light to rotate to the right.

2. Lævotartaric acid, which turns the plane of polarization to the left.

3. Inactive tartaric acid, which does not affect the plane of polarization.

4. Metatartaric acid.

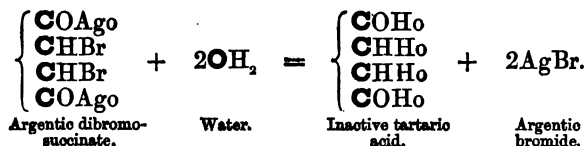
It has been already shown (p. 164) that dextrotartaric acid yields succinic acid under the influence of hydriodic acid, whilst it has also been ascertained that inactive tartaric acid likewise produces succinic acid under the same circumstances. These reactions indicate A. and B. to be the formulæ of the dextro- and inactive tartaric acids. The formulæ C. and D. possibly belong to lævo- and metatartaric acids, in which case these acids, when treated with hydriodic acid, ought to yield isosuccinic acid. Thus—



Racemic acid is a compound of dextro- and lævotartaric acid. It may be produced by uniting them, and may again be resolved into them.

Inactive tartaric acid cannot be resolved into dextro- and lævo-tartaric acids.

It may be obtained by the action of water on argentic dibromosuccinate:—

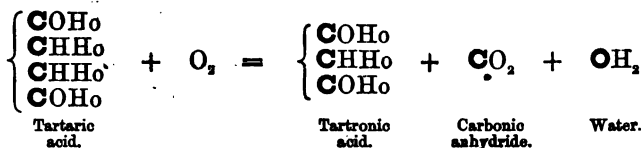


The converse of this reaction is the transformation of tartaric acid into succinic acid by means of hydriodic acid (see p. 164).

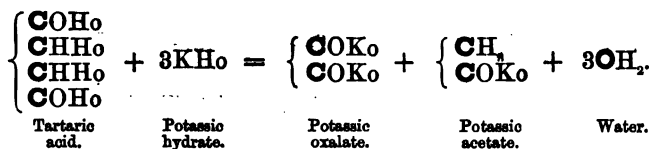
Metatartaric acid is produced by fusing dextrotartaric acid.

Reactions.—1. Dextrotartaric acid, when treated with powerful oxidizing agents, gives formic acid.

2. Under the influence of very gentle oxidizing agents, tartaric acid is formed:—

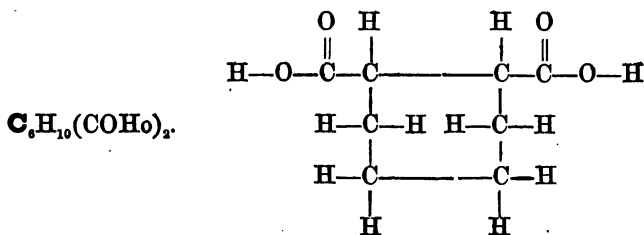


3. Heated with fused potassic hydrate, tartaric acid gives potassic oxalate and acetate, but without evolution of hydrogen:—

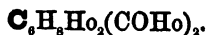
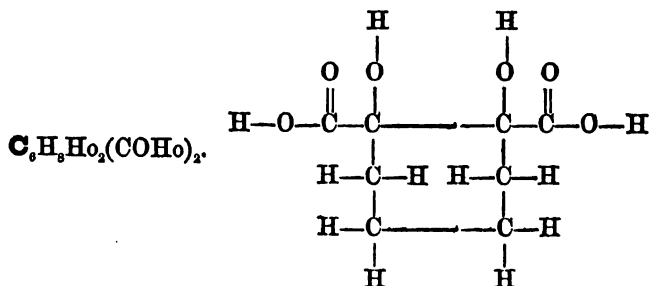


OTHER SERIES OF DIBASIC ACIDS.

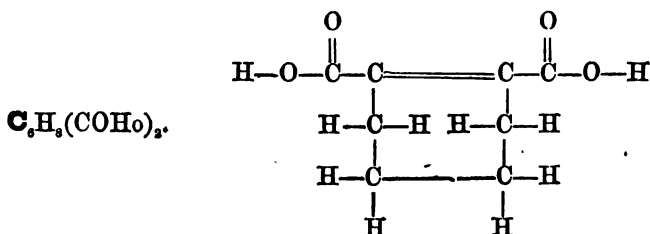
There is evidence of the existence of other series of dibasic acids, which may be regarded as derivatives of benzole or as the hexacarbon representatives of the succinic, fumaric, and tartaric series. The following are examples:—



Hexahydrophthalic acid (Hexacarbon-succinic series).

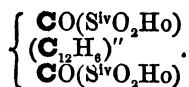


Tartrophthalic acid (Hexacarbon-tartaric series).

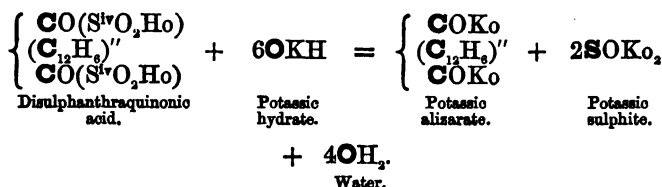


Tetrahydrophthalic acid (Hexacarbon-fumaric series).

The existence of another series of dibasic acids derived from hydrocarbons of a $\text{C}_n\text{H}_{2n-18}$ series is indicated by the formation of *anthraquinonic acid*, which is identical with *alizarin*, the chief colouring-matter of the madder root. By oxidation, *anthracene* ($\text{C}_{14}\text{H}_{10}$) yields *anthraquinone* ($\text{C}_{14}\text{H}_8\text{O}_2$), which, when heated strongly with sulphuric acid, is converted into *disulphanthraquinonic acid*, which has probably the following constitution:—



When disulphanthraquinonic acid is heated with potassic hydrate to a temperature of about 180°C ., it becomes intensely coloured, and is found to be converted into potassic alizarate (potassic anthraquinonate):—



On the addition of an acid to an aqueous solution of potassic alizarate, alizaric acid ($\text{C}_{12}\text{H}_6(\text{COHo})_2$), identical in properties with the natural alizarin of madder root, is precipitated.

Anthraflavic acid ($\text{C}_{12}\text{H}_6(\text{COHo})_2$), isomeric with alizaric acid, but possessing no tinctorial properties, is usually simultaneously formed in the above reactions.

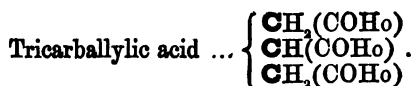
CHAPTER XXIV.

THE ACIDS.

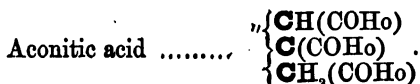
TRIBASIC ACIDS.

The tribasic acids all contain three semimolecules of oxatyl. They may be divided into the following three series, each series being, however, at present only represented by one acid.

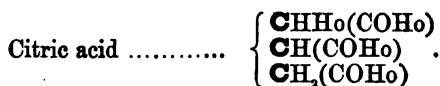
1. Tricarballic or acetoid series :—



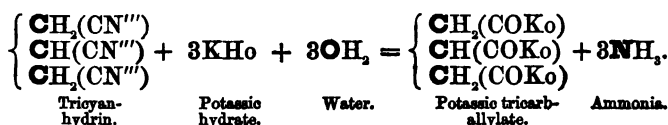
2. Aconitic or acryloid series :—



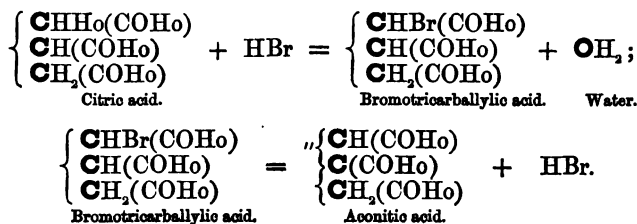
3. Citric or lactoid series :—



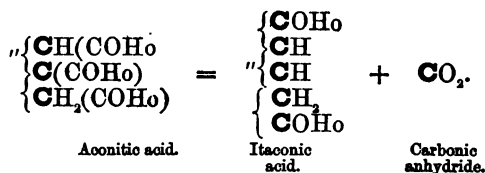
Tricarballic acid is trihydric. It is obtained from glycerin by replacing the hydroxyl in the latter by cyanogen, and then acting upon the tricyanhydrin, so formed, by potassic hydrate :—



Aconitic acid (equisetic acid, citridic acid) is also trihydric. It is found in the roots and leaves of monkshood, and may also be obtained by heating citric acid. Aconitic acid is also produced by the action of hydrobromic acid upon citric acid, the reaction taking place in the two following stages :—

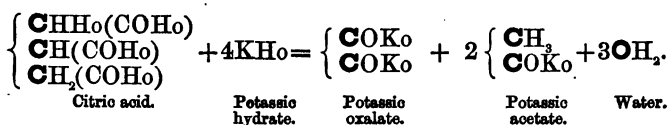


Heated to 160°, aconitic acid is converted into itaconic acid :—



Citric acid is tetrahydric, and contains, therefore, like lactic acid, one semimolecule of *non-oxatyllic* hydroxyl. It is found in the free state in oranges, lemons, citrons, and many other

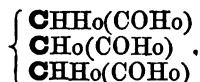
fruits, also in the potato and the onion. By the graduated application of heat, citric acid yields aconitic, itaconic, and citraconic acids. At the earlier stage of the decomposition it also yields acetone. Heated with fused potassic hydrate it gives potassic oxalate and acetate:—



By being heated with hydriodic acid, citric acid is transformed into tricarballic acid:—



Desoralic acid is closely connected with citric acid; it is hexahydric, and may be regarded as citric acid in which two atoms of *non-oxalylic* hydrogen have been replaced by hydroxyl. Its constitutional formula is probably

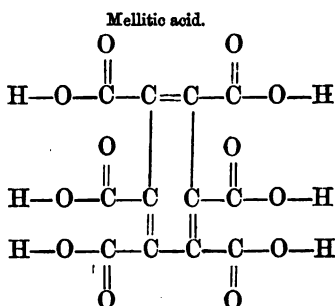


It is obtained from the product of the action of sodium upon oxalic ether.

TETRABASIC AND HEXABASIC ACIDS.

Pyromellitic acid ($\text{C}_6\text{H}_2(\text{COH}_0)_4$) and *mellitic acid* ($\text{C}_6(\text{COH}_0)_6$) are instances of acids of these degrees of basicity; and it can scarcely be doubted that an intermediate pentabasic acid will be found to exist. The following graphic formula of mellitic acid shows the relation of this acid to benzol, and indi-

cates the constitutional formulæ of the other acids built upon the same type and mentioned below :—



Five out of the six possible acids thus related to benzole are now known. Their names and formulæ are given in the following Table :—

| | | |
|-------------------------|---------------------------------------|---|
| Benzoic acid | $\text{C}_6\text{H}_5(\text{COHo})$. | |
| Phthalic acid..... | } | $\text{C}_6\text{H}_4(\text{COHo})_2$. |
| Isophthalic acid | | |
| Terephthalic acid | | |
| Trimellitic acid..... | } | $\text{C}_6\text{H}_3(\text{COHo})_3$. |
| Trimesic acid | | |
| Hemimellitic acid ... | | |
| Pyromellitic acid | } | $\text{C}_6\text{H}_2(\text{COHo})_4$. |
| Prehnitic acid | | |
| Mellophanic acid | | |
| Unknown acid | $\text{C}_6\text{H}(\text{COHo})_5$. | |
| Mellitic acid..... | $\text{C}_6(\text{COHo})_6$. | |

CHAPTER XXV.

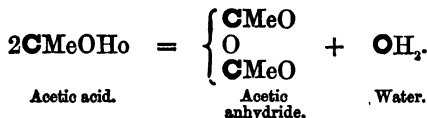
THE ANHYDRIDES.

THE anhydrides are compounds obtained from the acids by the abstraction of the hydrogen of their hydroxyl, together with sufficient oxygen to form water.

• For every two atoms of hydrogen and one of oxygen thus abstracted from hydroxyl, there will obviously remain one atom of oxygen, which, as a dyad element, exactly satisfies the two bonds vacated by the hydroxyl :—



On this account, two molecules of a monohydric acid are required to form one molecule of anhydride, thus :—



The anhydrides of those monobasic and dibasic acids which contain one and two semimolecules of hydroxyl have alone been investigated.

They may be divided into the following classes :—

1. Anhydrides of the monohydric monobasic acids $\left\{ \begin{array}{c} \text{C}_n\text{H}_{2n+1} \\ \text{CO} \\ \text{O} \\ \text{CO} \\ \text{C}_n\text{H}_{2n+1} \end{array} \right.$ and $\left\{ \begin{array}{c} \text{C}_n\text{H}_{2n-7} \\ \text{CO} \\ \text{O} \\ \text{CO} \\ \text{C}_n\text{H}_{2n-7} \end{array} \right.$.
2. Anhydrides of the dihydric monobasic acids $\left\{ \begin{array}{c} \text{C}(\text{C}_n\text{H}_{2n+1})_2 \\ \text{CO} \end{array} \right. \text{O}.$
3. Anhydrides of the dihydric dibasic acids $\left\{ \begin{array}{c} \text{CO} \\ \text{C}_n\text{H}_{2n} \\ \text{CO} \end{array} \right. \text{O}.$

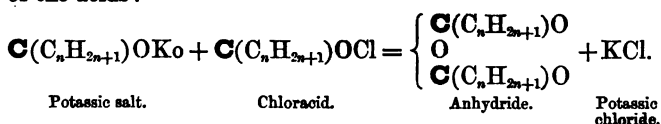
1. ANHYDRIDES OF THE MONOHYDRIC MONOBASIC ACIDS.

These are known only in the acetic and benzoic series.

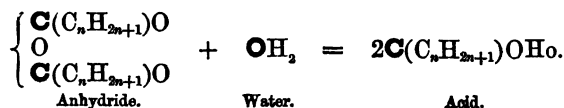
They bear the same relation to the acids from which they are derived as that borne by the ethers to the alcohols.

The residues of different acids unite to form mixed anhydrides analogous to the mixed ethers. Aceto-benzoic anhydride is a body of this class.

Formation.—By the action of the chloracids, or so-called chlorides of the monad negative radicals, on the potassic salts of the acids :—



Reaction. In contact with water they are converted into the corresponding acids :—



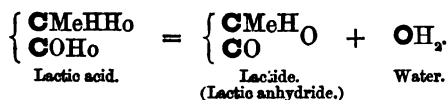
The following is a list of the anhydrides belonging to this class :—

| | | | Fusing-point. | Boiling point. |
|-------------------------|---|--|---------------|----------------|
| Acetic anhydride | $\left\{ \begin{array}{c} \text{CMeO} \\ \text{O} \\ \text{CMeO} \end{array} \right.$ | or $\left\{ \begin{array}{c} \text{C}(\text{CH}_3)\text{O} \\ \text{O} \\ \text{C}(\text{CH}_3)\text{O} \end{array} \right.$ | — | 138°. |
| Propionic anhydride ... | $\left\{ \begin{array}{c} \text{CEtO} \\ \text{O} \\ \text{CEtO} \end{array} \right.$ | or $\left\{ \begin{array}{c} \text{C}(\text{C}_2\text{H}_5)\text{O} \\ \text{O} \\ \text{C}(\text{C}_2\text{H}_5)\text{O} \end{array} \right.$ | — | 165°. |
| Butyric anhydride | $\left\{ \begin{array}{c} \text{CPrO} \\ \text{O} \\ \text{CPrO} \end{array} \right.$ | or $\left\{ \begin{array}{c} \text{C}(\text{C}_3\text{H}_7)\text{O} \\ \text{O} \\ \text{C}(\text{C}_3\text{H}_7)\text{O} \end{array} \right.$ | — | about 190°. |
| Valeric anhydride | $\left\{ \begin{array}{c} \text{CBuO} \\ \text{O} \\ \text{CBuO} \end{array} \right.$ | or $\left\{ \begin{array}{c} \text{C}(\text{C}_4\text{H}_9)\text{O} \\ \text{O} \\ \text{C}(\text{C}_4\text{H}_9)\text{O} \end{array} \right.$ | — | about 215°. |

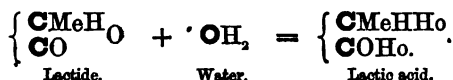
| | | Fusing-point. | Boiling-point. |
|-------------------------|--|---------------|----------------|
| Caproic anhydride..... | $\begin{cases} \text{CAyO} \\ \text{O} \\ \text{CAyO} \end{cases}$ or $\begin{cases} \text{C}(\text{C}_6\text{H}_{11})\text{O} \\ \text{O} \\ \text{C}(\text{C}_6\text{H}_{11})\text{O} \end{cases}$ | — | — |
| Enanthylic anhydride. | $\begin{cases} \text{CCpO} \\ \text{O} \\ \text{CCpO} \end{cases}$ or $\begin{cases} \text{C}(\text{C}_8\text{H}_{13})\text{O} \\ \text{O} \\ \text{C}(\text{C}_8\text{H}_{13})\text{O} \end{cases}$ | 42°. | 310°. |
| Benzoic anhydride..... | $\begin{cases} \text{C}(\text{C}_6\text{H}_5)\text{O} \\ \text{O} \\ \text{C}(\text{C}_6\text{H}_5)\text{O} \end{cases}$ | — | — |
| Acetobenzoic anhydride | $\begin{cases} \text{CMeO} \\ \text{O} \\ \text{C}(\text{C}_6\text{H}_5)\text{O} \end{cases}$ | — | 120°. |
| Caprylic anhydride ... | $\begin{cases} \text{C}(\text{C}_7\text{H}_{15})\text{O} \\ \text{O} \\ \text{C}(\text{C}_7\text{H}_{15})\text{O} \end{cases}$ | below 0°. | about 290°. |
| Pelargonic anhydride. . | $\begin{cases} \text{C}(\text{C}_9\text{H}_{17})\text{O} \\ \text{O} \\ \text{C}(\text{C}_9\text{H}_{17})\text{O} \end{cases}$ | +5°. | — |
| Palmitic anhydride ... | $\begin{cases} \text{C}(\text{C}_{15}\text{H}_{31})\text{O} \\ \text{O} \\ \text{C}(\text{C}_{15}\text{H}_{31})\text{O} \end{cases}$ | 53°8. | — |

2. ANHYDRIDES OF THE DIHYDRIC MONOBASIC ACIDS.

Formation.—By applying heat to a dihydric monobasic acid, thus :—

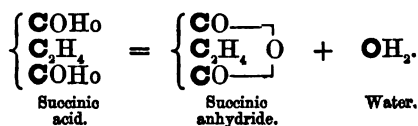


Reaction.—Boiled with water, and especially with alkalis, they reproduce the acids from which they were derived :—



3. ANHYDRIDES OF THE DIHYDRIC DIBASIC ACIDS.

Formation.—By the action of heat, or of substances having a strong affinity for water, upon the dihydric dibasic acids:—



Reaction.—Like the anhydrides of the first and second classes, they unite with water, reproducing the acids from which they were derived.

CHAPTER XXVI.

THE KETONES.

THE ketones are derived from the fatty acids by the substitution of the hydroxyl of the latter by a monad positive radical; they thus resemble the aldehydes in constitution:—

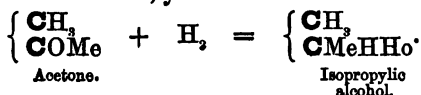


The ketones may also be correctly described as compounds of carbonic oxide with monad positive radicals, thus:—



By the action of nascent hydrogen upon the ketones, they

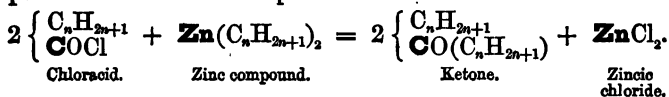
are converted into secondary alcohols, whilst the aldehydes, under the same treatment, yield normal alcohols :—



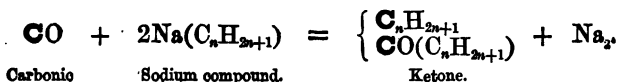
Ketones, unlike aldehydes, do not oxidize spontaneously; neither do they reduce ammoniacal solution of argentic oxide.

Like aldehydes, many of them combine with hydric potassic or hydric sodic sulphite.

Formation.—1. By the action of the zinc compounds of the positive monad radicals upon chloracids :—



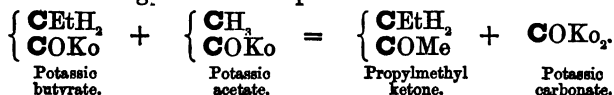
2. By the action of sodic ethide and its homologues on carbonic oxide :—



3. By the distillation of the salts of the fatty acids :—

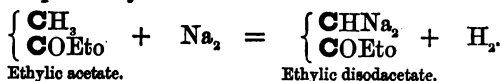


4. By distilling together salts of two different fatty acids, ketones containing two different positive radicals are obtained :—

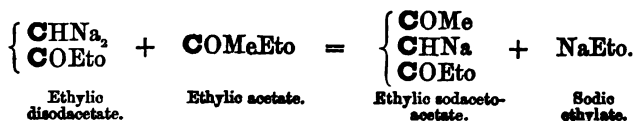


5. Numerous ketones may also be produced by the following series of reactions.

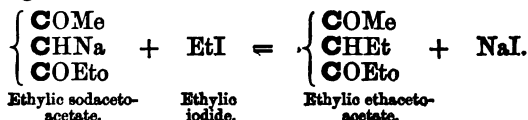
By the action of sodium upon ethylic acetate hydrogen becomes replaced by sodium :—



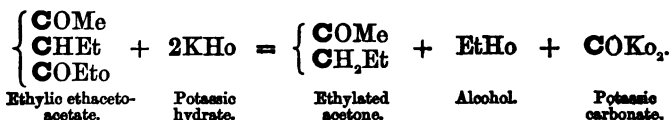
The ethylic disodacetate is acted upon by excess of ethylic acetate as follows:—



When ethylic iodide is added to ethylic sodacetate the following reaction occurs:—

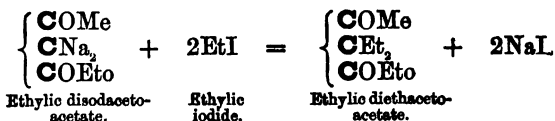
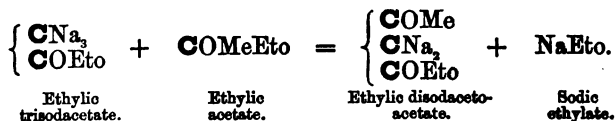
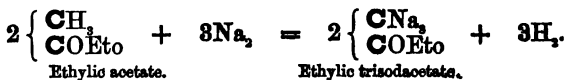


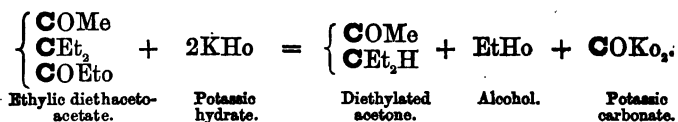
Lastly, ebullition of ethylic ethacetate with potassic hydrate converts it into ethylated acetone, alcohol, and potassic carbonate:—



Ethylated acetone is obviously acetone in which one atom of hydrogen has been replaced by ethyl.

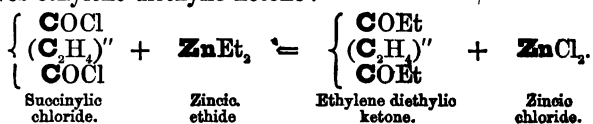
A second atom of hydrogen in acetone may be replaced in the following analogous series of reactions:—





6. By the action of zincic ethide on the chlorides obtained from the dibasic acids, ketones containing dyad radicals are produced; thus:—

Succinylic chloride submitted to the action of zincic ethide gives ethylene diethylic ketone:—



The following is a list of the names, constitutional formulæ, and boiling-points of those ketones which are best known:—

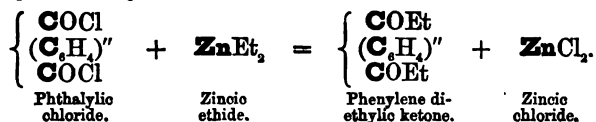
| | | | Boiling- point. |
|-----------|---|--|--------------------|
| | Acetone | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{COMe} \end{array} \right.$ | 56°. |
| | Methylated acetone. (<i>Ethyl acetyl, methyl acetone.</i>) | $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{COMe} \end{array} \right.$ | 81°. |
| Isomeric. | Dimethylated acetone. (<i>Ethyl acetone.</i>) | $\left\{ \begin{array}{l} \text{CMe}_2\text{H} \\ \text{COMe} \end{array} \right.$ | 93°·5 |
| | Ethylated acetone ... | $\left\{ \begin{array}{l} \text{CEtH}_2 \\ \text{COMe} \end{array} \right.$ | 101°. |
| | Propione. (<i>Ethyl propionyl.</i>) | $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{COEt} \end{array} \right.$ | 101°. |
| Isomeric. | Methyl valeral | $\left\{ \begin{array}{l} \text{CPrH}_2 \\ \text{COMe} \end{array} \right.$ | 120°. |
| | Ethyl butyral | $\left\{ \begin{array}{l} \text{CEtH}_2 \\ \text{COEt} \end{array} \right.$ | 128°. |
| Isomeric. | Diethylated acetone | $\left\{ \begin{array}{l} \text{CEt}_2\text{H} \\ \text{COMe} \end{array} \right.$ | 138°. |
| | Butyrone | $\left\{ \begin{array}{l} \text{CEtH}_2 \\ \text{COPr} \end{array} \right.$ | 144°. |

Little is known of the ketones of the C_nH_{2n-7} series. The following have been obtained :—

Benzophenone $\left(\left\{ \begin{smallmatrix} CH_3 \\ CO(C_6H_5) \end{smallmatrix} \right\} \right)$, the ketone of benzoic acid, is obtained by heating potassic benzoate.

Methyl benzole or *methyl benzoyl* $\left(\left\{ \begin{smallmatrix} CH_3 \\ CO(C_6H_5) \end{smallmatrix} \right\} \right)$ is prepared by distilling together calcic acetate and benzoate.

Phthalyl chloride, treated with zincic ethide, produces *phenylene diethylic ketone* :—



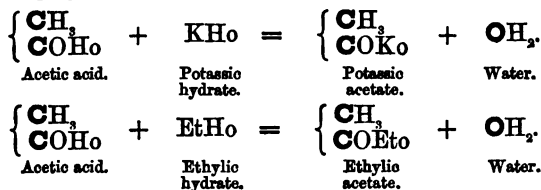
CHAPTER XXVII.

ETHEREAL SALTS.

THESE compounds correspond to the metallic oxysalts of the acids.

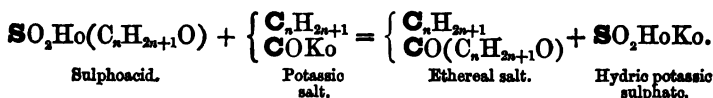
The acids from which they are derived may be either mineral or organic; but the base must always be organic. The haloid ethereal salts are excluded from this family; they have been already described as haloid ethers.

The ethereal salts are produced by reactions analogous to those employed for the preparation of metallic salts :—



But as the hydrates of the organic radicals do not act upon acids so energetically as potassic hydrate, it is often advisable

to employ the acid in the form of a potassic salt, and the radical as a sulphoacid; thus, with acids of the acetic series:—



Monobasic acids form only one ethereal salt with each monohydric alcohol; and this salt is always normal.

With dihydric alcohols they each form two ethereal salts, and with trihydric alcohols three ethereal salts. These are also normal. Thus with acetic acid we have:—

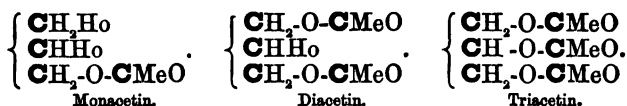
Acetic salt of a monohydric alcohol:—



Acetic salts of a dihydric alcohol:—

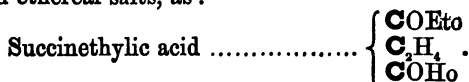


Acetic salts of a trihydric alcohol:—

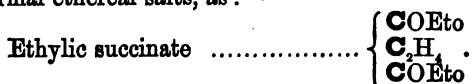


Dibasic acids form, with monohydric alcohols, two series of ethereal salts:—

1. Acid ethereal salts, as:—

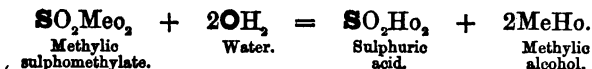


2. Normal ethereal salts, as:—

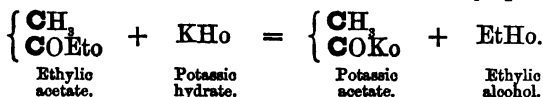


In the same manner, tribasic acids form with monohydric alcohols three series of ethereal salts, the first two of which are acid, and the third normal.

Prolonged contact with water generally decomposes ethereal salts, liberating the radicals of the bases in the form of alcohols :—



Ebullition with potassic hydrate, especially when the latter is dissolved in alcohol, effects this transformation very speedily :—



CHAPTER XXVIII.

ORGANIC COMPOUNDS CONTAINING TRIAD AND PENTAD NITROGEN OR THEIR ANALOGUES.

THIS numerous family may be divided into two great classes :—

1. Compounds of triad nitrogen, phosphorus, arsenic, antimony, and bismuth.
2. Compounds of pentad nitrogen, phosphorus, arsenic, antimony, and bismuth.

I. COMPOUNDS OF TRIAD NITROGEN AND OF ITS ANALOGUES.

This class may be again subdivided as follows :—

| Positive. | Neutral. | Negative. |
|-----------------|-----------------------|---------------|
| 1. Amines. | 1. Amides. | 1. Imides and |
| 2. Phosphines. | 2. Alkalamides. | nitrides of |
| 3. Arsines. | 3. Trichlorinated and | negative |
| | tribrominated amines. | radicals. |
| 4. Stibines. | 4. Haloid compounds | |
| 5. Bismuthines. | of oxybases. | |
| 6. Oxybases. | | |

Of these the Amines and Amides are the most important.

POSITIVE SECTION.

1. *THE AMINES.*

The Amines are commonly termed organic bases or artificial alkaloids; they are divided into—

- A. Monamines.
- B. Diamines.
- C. Triamines.
- D. Tetramines.

The tetramines have been but little investigated.

A. *MONAMINES.*

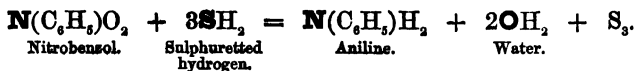
There are three kinds of monamines :—

- α. Primary monamines.
- β. Secondary monamines.
- γ. Tertiary monamines.

α. *Primary Monamines.*

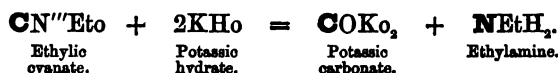
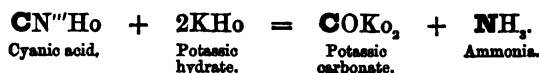
| | General formulæ. |
|--------------------------------------|-----------------------|
| Methyl or C_nH_{2n+1} series..... | $N(C_nH_{2n+1})H_2$. |
| Vinyl or C_nH_{2n-1} series | $N(C_nH_{2n-1})H_2$. |
| Phenyl or C_nH_{2n-7} series | $N(C_nH_{2n-7})H_2$. |

Formation.—1. By the reduction of the nitro-substitution compounds of the hydrides of the positive radicals by sulphuretted hydrogen, ammoniac sulphide, zinc and sulphuric acid, or iron and acetic acid :—

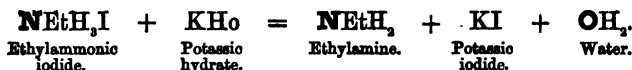
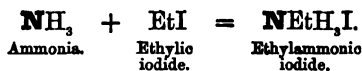


2. By treating cyanic ethers with boiling solution of potassic

hydrate. The reaction is perfectly analogous to the decomposition of cyanic acid with potassic hydrate:—



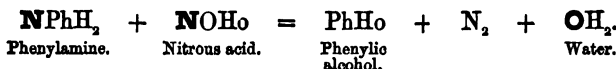
3. By the action of the haloid compounds of the monad positive radicals upon ammonia, and subsequent action of potassic hydrate upon the product so formed:—



The following are a few of the primary monamines:—

| | |
|---------------------------------|--|
| Methylamine..... | NMeH_2 or $\text{N}(\text{CH}_3)_2$. |
| Ethylamine | NEtH_2 or $\text{N}(\text{C}_2\text{H}_5)_2$. |
| Butylamine | NBuH_2 or $\text{N}(\text{C}_4\text{H}_9)_2$. |
| Amylamine | NAyH_2 or $\text{N}(\text{C}_5\text{H}_{11})_2$. |
| Allylamine..... | NAlH_2 or $\text{N}(\text{C}_3\text{H}_5)_2$. |
| Phenylamine (<i>Aniline</i>) | NPhH_2 or $\text{N}(\text{C}_6\text{H}_5)_2$. |
| Tolylamine (<i>Toluidine</i>) | NToH_2 or $\text{N}(\text{C}_6\text{H}_4\text{Me})_2$. |

Reactions.—Treated with nitrous acid, they evolve nitrogen and yield the corresponding alcohols:—

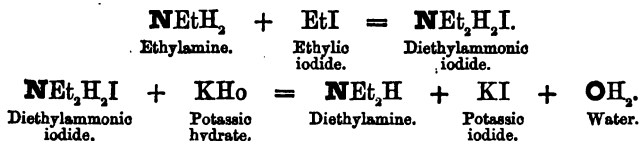


β. Secondary Monamines.

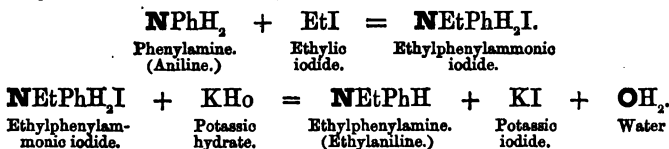
| | |
|--|---|
| | General formulæ. |
| Methyl or $\text{C}_n\text{H}_{2n+1}$ series | $\text{N}(\text{C}_n\text{H}_{2n+1})_2$. |
| Vinyl or $\text{C}_n\text{H}_{2n-1}$ series..... | $\text{N}(\text{C}_n\text{H}_{2n-1})_2$. |
| Phenyl or $\text{C}_n\text{H}_{2n-7}$ series | $\text{N}(\text{C}_n\text{H}_{2n-7})_2$. |

The secondary monamines are derived from ammonia by the replacement of two atoms of hydrogen by monad positive radicals. They are sometimes called *Imidogen bases*.

Formation.—By the action of the haloid compounds of the monad positive radicals on the primary monamines, and subsequent treatment with potassic hydrate:—



By using the iodide of a radical different from that already contained in the primary monamine, secondary monamines may be formed containing two different radicals, thus:—



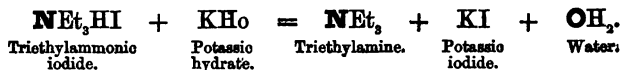
The following secondary monamines are known:—

| | | | |
|------------------------|--------------------------------------|----|--|
| Dimethylamine..... | NMe ₂ H | or | N(CH ₃) ₂ H. |
| Diethylamine | NEt ₂ H | or | N(C ₂ H ₅) ₂ H. |
| Methylethylamine | NMeEtH | or | N(CH ₃)(C ₂ H ₅)H. |
| Dibutylamine | NBu ₂ H | or | N(C ₄ H ₉) ₂ H. |
| Ethylamylamine | NEtAyH | or | N(C ₂ H ₅)(C ₅ H ₁₁)H. |
| Ethylphenylamine | NEtPhH | or | N(C ₂ H ₅)(C ₆ H ₅)H. |
| Piperidine | N(C ₄ H ₁₀)H. | | |
| Conine..... | N(C ₅ H ₁₁)H. | | |

γ. Tertiary Monamines.

Formation.—1. By acting upon the secondary monamines with the iodides of the monad positive radicals, and subsequently treating the product with potassic hydrate:—



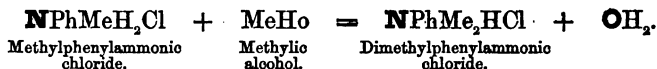
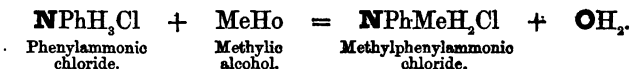


By varying the radicals, tertiary monamines with several different radicals may be formed. The following are a few of the known tertiary monamines:—

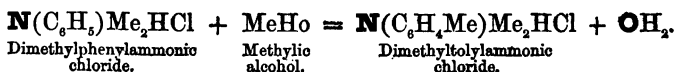
| | |
|--------------------------|---|
| Trimethylamine | NMe_3 or $\text{N}(\text{CH}_3)_3$. |
| Triethylamine | NEt_3 or $\text{N}(\text{C}_2\text{H}_5)_3$. |
| Tributylamine | NBu_3 or $\text{N}(\text{C}_4\text{H}_9)_3$. |
| Triamylamine | NAy_3 or $\text{N}(\text{C}_5\text{H}_{11})_3$. |
| Methyl-ethyl-phenylamine | NMeEtPh or $\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)$. |
| Pyridine | $\text{N}(\text{C}_5\text{H}_5)'''$. |
| Picoline | $\text{N}(\text{C}_6\text{H}_7)'''$. |
| Lutidine | $\text{N}(\text{C}_8\text{H}_9)'''$. |
| Collidine | $\text{N}(\text{C}_9\text{H}_{11})'''$. |
| Parvoline | $\text{N}(\text{C}_9\text{H}_{13})'''$. |

The constitution of the triad radicals contained in the last five bases is not known.

2. When phenylammonio chloride (aniline hydrochlorate) and methylic alcohol are digested together at from 280° to 300° , the non-phenylic hydrogen becomes replaced by methyl, thus:—



By continuing the digestion longer, the phenylic hydrogen is also replaced by methyl according to the following reaction:—



By these reactions the following tertiary monamines have been produced:—

| | |
|--------------------------|--|
| Dimethylaniline | $\text{N}(\text{C}_6\text{H}_5)_3\text{Me}_2$. |
| Dimethyltoluidine | $\text{N}(\text{C}_6\text{H}_4\text{Me})\text{Me}_2$. |
| Dimethylxylylidine | $\text{N}(\text{C}_6\text{H}_3\text{Me}_2)\text{Me}_2$. |
| Dimethylcumidine | $\text{N}(\text{C}_6\text{H}_2\text{Me}_3)\text{Me}_2$. |
| Dimethyleymidine | $\text{N}(\text{C}_6\text{HMe})\text{Me}_2$. |

The final product which may be expected to result from this reaction, $\text{N}(\text{C}_6\text{Me}_5)_3$, has not yet been obtained.

Tertiary monamines, when acted upon by the iodides of monad positive radicals, yield iodides which are not decomposed by potassic hydrate. In this manner tertiary monamines may be distinguished from primary and secondary monamines. The three may be distinguished from each other by the alternate action of ethylic iodide and potassic hydrate: thus, as we have just seen, tertiary monamines are recognized by producing immediately iodides which are not decomposed by potassic hydrate; a secondary monamine, however, produces an iodide decomposable by potassic hydrate; but the base thus liberated is tertiary, and will therefore be transformed immediately into the stable iodide by a second application of ethylic iodide. A primary monamine requires three applications of ethylic iodide and potassic hydrate to produce the same result.

B. DIAMINES.

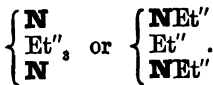
Formation.—The diamines are formed by coupling together two atoms of nitrogen in two molecules of ammonia, or of a primary or secondary monamine, by a dyad radical, which at the same time takes the place of two atoms of hydrogen; thus:—



Primary
diamine.



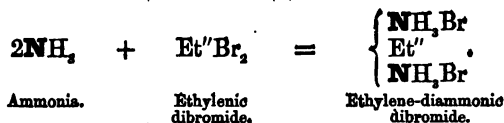
Secondary
diamine.



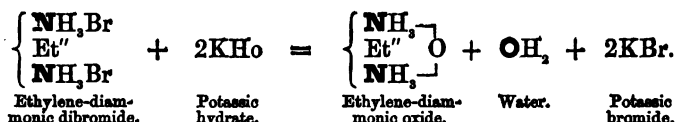
Tertiary diamine.

196 COMPOUNDS OF NITROGEN AND ITS ANALOGUES.

This reaction is effected by treating ammonia or a primary or secondary monamine with the haloid salt (preferably a bromide) of the dyad radical, thus :—



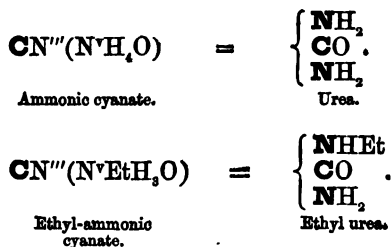
When the salts of ethylene diammonium are decomposed by potassic hydrate, an oxide of the compound nitrogenous radical is produced, thus :—



In this respect most of the diamines differ from the monamines.

Urea and its derivatives belong to the class of diamines.

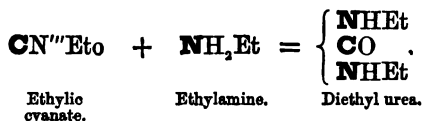
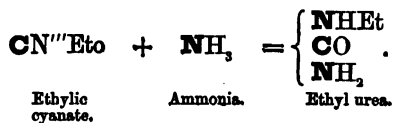
These compounds are produced by boiling a solution of ammonic cyanate or ethylammonic cyanate, or a homologue of the latter. In these compounds, the two atoms of nitrogen are held together by the dyad radical carbonyl, CO :—



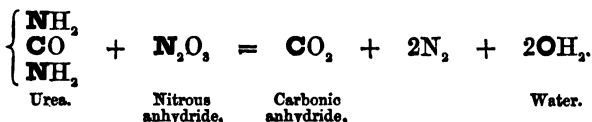
By heating ammonic carbonate to 130°–140° in closed vessels for a few hours, urea is produced :—



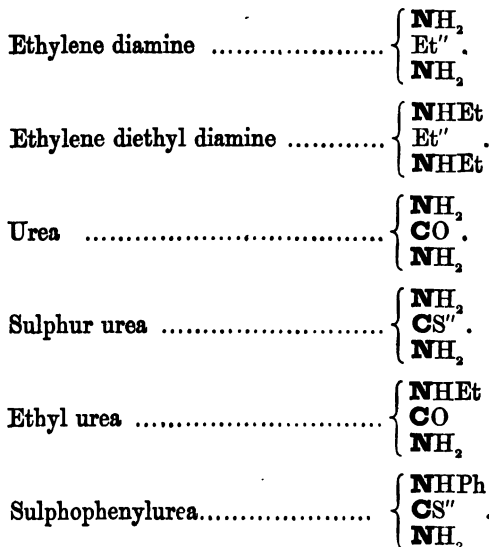
Ureas in which ethyl and other monad positive radicals are substituted for hydrogen may also be obtained by the action of ammonia or a monamine on the cyanic ethers, thus:—



Reaction.—Urea is decomposed by nitrous anhydride:—

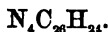


The following is a list of the best-known diamines:—

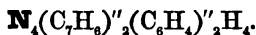


C. TRIAMINES.

To this class of organic bases belong many of the aniline colours and their derivatives. *Mauveine* was the first discovered of these bodies; it is obtained by the action of concentrated sulphuric acid and red potassic chromate upon aniline. It is also produced by heating the coloured product obtained by the action of a solution of bleaching powder upon aniline. The molecular formula of mauveine is



It is probably a tetramine with the constitution shown in the following formula:—

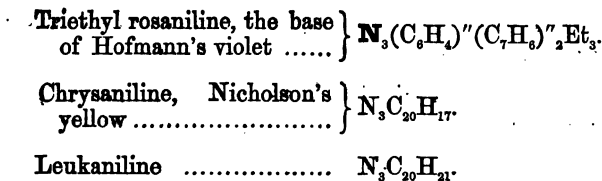


Rosaniline is obtained from a mixture of aniline and toluidine by the action of various reagents, such as carbonic chloride, stannic chloride, mercuric chloride, ferric chloride, cupric chloride, the sulphuric and nitric salts of tin and mercury, and, lastly, arsenic acid which has superseded all other reagents for the technical preparation of the salts of this base.

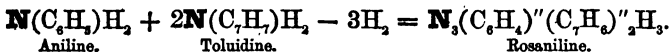
By the replacement of hydrogen in rosaniline by positive radicals, other bases, forming with acids valuable colouring-matters, are produced.

The following is a list of the best-known of these bases:—

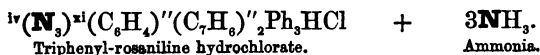
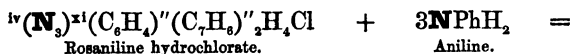
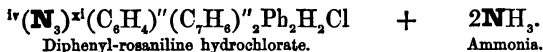
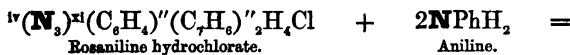
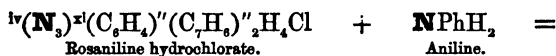
| | |
|---|---|
| Rosaniline, the base of magenta | } $\text{N}_3(\text{C}_6\text{H}_4)''(\text{C}_7\text{H}_8)''_2\text{H}_3.$ |
| Phenyl rosaniline, the base of dahline | } $\text{N}_3(\text{C}_6\text{H}_4)''(\text{C}_7\text{H}_8)''_2\text{PhH}_2.$ |
| Diphenyl rosaniline, the base of aniline violet | } $\text{N}_3(\text{C}_6\text{H}_4)''(\text{C}_7\text{H}_8)''_2\text{Ph}_2\text{H}.$ |
| Triphenyl rosaniline, the base of aniline blue | } $\text{N}_3(\text{C}_6\text{H}_4)''(\text{C}_7\text{H}_8)''_2\text{Ph}_3.$ |
| Tritolyl rosaniline, the base of toluidine blue | } $\text{N}_3(\text{C}_6\text{H}_4)''(\text{C}_7\text{H}_8)''_2(\text{C}_7\text{H}_7)_3.$ |



Rosaniline appears to be formed by the abstraction of three molecules of hydrogen from one molecule of aniline and two molecules of toluidine, thus:—



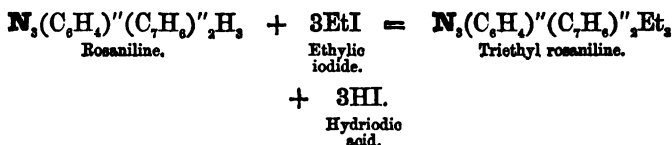
The phenyl derivatives of rosaniline are produced as salts of hydrochloric acid by heating rosaniline hydrochlorate with various proportions of aniline, thus:—



The salts of tritolyl rosaniline are formed by analogous reactions.

Triethyl rosaniline is obtained by heating to 100°, in a

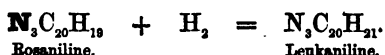
close vessel, rosaniline with ethylic iodide dissolved in alcohol:—



Trimethyl and triamyl rosaniline are obtained by analogous processes.

Chrysaniline is formed as a secondary product in the manufacture of rosaniline.

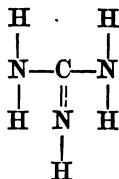
Leukaniline is produced by the action of zinc upon an acid solution of rosaniline:—



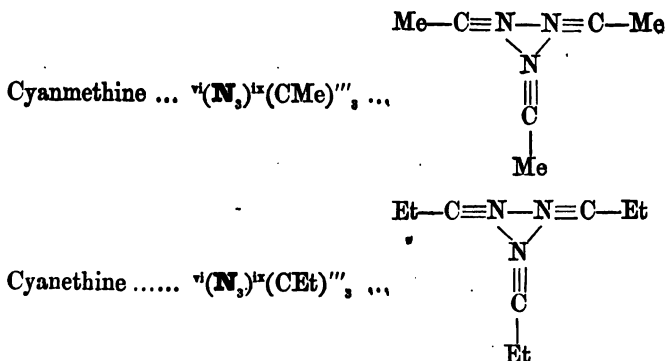
OTHER AMINES.

Subjoined are the names and formulæ of a number of organic bases which cannot at present be satisfactorily classified:—

| | |
|----------------|---|
| Guanine | $\text{C}_5\text{H}_5\text{N}_5\text{O}.$ |
| Guanidine..... | $\text{C}(\text{NH})''(\text{NH}_2)(\text{NH}_2)$ or $\text{C}(\text{NH})''\text{Ad}_2.$ |



| | |
|---------------------|---|
| Furfurine | $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_3.$ |
| Amarine | $\text{C}_{21}\text{H}_{18}\text{N}_2.$ |
| Thialdine | $\text{C}_6\text{H}_{13}\text{NS}_2.$ |
| Dibutyraldine | $\text{C}_8\text{H}_{17}\text{NO}.$ |
| Acridine | $\text{C}_{24}\text{H}_{18}\text{N}_2.$ |



THE NATURAL ALKALOIDS.

Of the constitution of these organic bases very little is known. The following is a list of the chief of them, with the sources whence they are derived:—

Alkaloids from Opium.

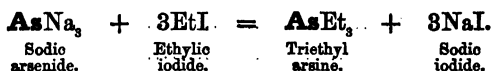
| | |
|----------------------|---|
| Hydrocotarnine | $\text{C}_{12}\text{H}_{15}\text{NO}_3$. |
| Morphine | $\text{C}_{17}\text{H}_{19}\text{NO}_3$. |
| Codeine..... | $\text{C}_{18}\text{H}_{21}\text{NO}_3$, OH_2 . |
| Thebaine | $\text{C}_{19}\text{H}_{21}\text{NO}_3$. |
| Protopine | $\text{C}_{20}\text{H}_{19}\text{NO}_5$. |
| Papaverine | $\text{C}_{20}\text{H}_{21}\text{NO}_4$. |
| Cryptopine | $\text{C}_{21}\text{H}_{23}\text{NO}_5$. |
| Laudanosine..... | $\text{C}_{21}\text{H}_{27}\text{NO}_4$. |
| Narcotine | $\text{C}_{22}\text{H}_{23}\text{NO}_7$. |
| Narceine | $\text{C}_{23}\text{H}_{29}\text{NO}_6$. |

From Cinchona Bark.

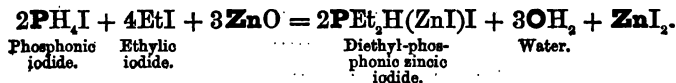
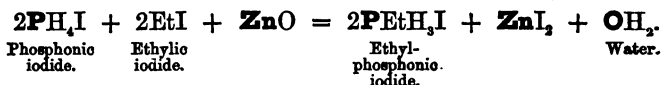
| | |
|------------------|--|
| Quinine..... | $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$. |
| Cinchonine | $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}$. |
| Aricine | $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4$. |

*From Nightshade.*Atropine $C_{17}H_{23}NO_3$.*From Tobacco.*Nicotine $C_{10}H_{14}N_2$.*From Nux vomica.*Strychnine $C_{21}H_{22}N_2O_2$.Brucine..... $C_{23}H_{28}N_2O_4$.*From Tea, Coffee, and Cocoa.*Theobromine $C_7H_8N_4O_2$.Caffeine (*Theine*)..... $C_8H_{10}N_4O_2$.2, 3, 4. *THE PHOSPHINES, ARSINES, STIBINES,
AND BISMUTHINES.*

The bases containing phosphorus may be obtained, like the amines, by the displacement of hydrogen in phosphuretted hydrogen. The tertiary compounds only of arsenic, antimony, and bismuth are known; and they are produced by reactions of which the following may be regarded as a type:—



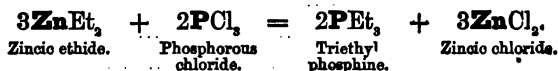
Primary and secondary phosphines are obtained by the action of methylic or ethylic iodide and zincic oxide upon phosphonic iodide. With ethylic iodide the following reactions occur:—



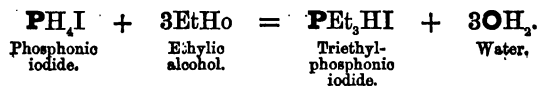
These reactions take place side by side; but the primary and secondary phosphines are readily separated from each other by the consecutive action of water and alkalies upon the products of the above operation.

The addition of water to the mixed product liberates the primary phosphine from its compound, whilst the compound of the secondary phosphine resists even boiling water, but easily decomposes under the influence of alkalies.

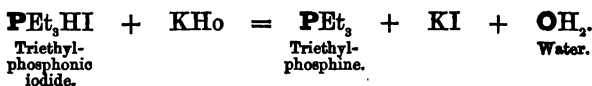
The tertiary phosphines are produced by the action of the zinc compounds of the monad positive radicals upon phosphorous chloride:—



They may also be obtained in combination with hydriodic acid by the action of phosphonic iodide upon the alcohols:—



By the action of alkalies upon triethyl-phosphonic iodide triethyl phosphine is liberated:—



The following Table contains the names of the known phosphines, arsines, and stibines:—

Primary Phosphines.

| | Formula. | Boiling-point. |
|------------------------|-----------------------|----------------|
| Methyl phosphine | PMeH_2 | —14°. |
| Ethyl phosphine | PEtH_2 | 25°. |

Secondary Phosphines.

| | | |
|--------------------------|------------------------------|------|
| Dimethyl phosphine | PMe_2H | 25°. |
| Diethyl phosphine | PEt_2H | 85°. |

Tertiary Phosphines.

| | Formula. | Boiling-point. |
|---------------------------|------------------------------|----------------|
| Trimethyl phosphine | PMe₃ | 41°. |
| Triethyl phosphine | PEt₃ | 127°·5. |

Tertiary Arsines.

| | | |
|------------------------|-------------------------------|-------|
| Trimethyl arsine | AsMe₃ | 120°. |
| Triethyl arsine..... | AsEt₃ | 140°. |

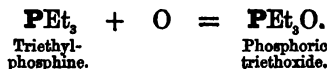
Tertiary Stibines.

| | | |
|-------------------------|-------------------------------|-------|
| Trimethyl stibine | SbMe₃ | — |
| Triethyl stibine | SbEt₃ | 158°. |
| Triamyl stibine | SbAy₃ | — |

Tertiary Bismuthine.

| | | |
|---------------------------|-------------------------------|---|
| Triethyl bismuthine | BiEt₃ | — |
|---------------------------|-------------------------------|---|

Character.—The phosphines, arsines, stibines, and bismuthines possess very energetic affinities for negative elements. Many of them are spontaneously inflammable in air and oxygen. Most, probably all, unite with an atom of oxygen or a molecule of chlorine, bromine, or iodine, forming compounds in which the grouping element becomes pentadic. Thus, by the absorption of oxygen, triethyl-phosphine is transformed into phosphoric triethoxide:—



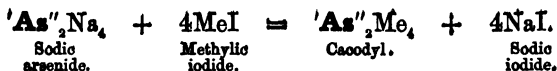
5. OXYBASES.

These compounds are only known in the arsenic series.

Arsenious oxybases.

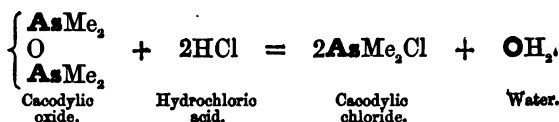
Only one of these, cacodylic oxide, has been carefully investigated.

By the distillation of potassic acetate with arsenious anhydride, a compound known as cacodyl, ' As_2Me_2 ', is produced. This substance may also be prepared by the action of methylic iodide upon an alloy of sodium and arsenic containing ' As_2Na_4 ':—



By allowing cacodyl to absorb oxygen slowly, an oily liquid containing cacodylic oxide ($\text{As}_2\text{Me}_2\text{O}$) is formed.

This oxybase does not appear to unite with oxygen acids, but it is attacked by hydrochloric acid, forming cacodylic chloride:—



Cacodylic oxide, when exposed to moist air, absorbs water and oxygen, forming cacodylic acid:—



CHAPTER XXIX.

ORGANIC COMPOUNDS OF TRIAD NITROGEN AND OF ITS ANALOGUES (*continued*).

NEUTRAL SECTION.

1. THE AMIDES.

These compounds are formed by the substitution of amidogen (NH_2) for the oxytylic hydroxyl of organic acids. They are

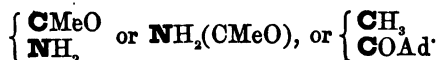
most conveniently written on the diadelphic type, but may also be formulated upon the ammonia type.

If the acid contain only one semimolecule of oxatyl, a monamide is the result; if two semimolecules of oxatyl are present in the acid, a diamide is generally formed, &c. Secondary and tertiary compounds can also be produced, as in the case of the amines; but they belong to the negative section of this family.

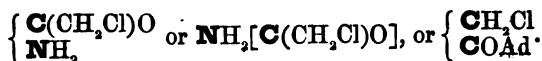
A. MONAMIDES.

I. Primary Monamides.

Acetamide:—



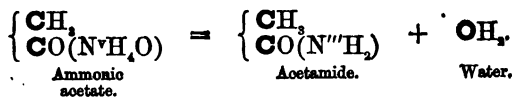
Chloracetamide:—



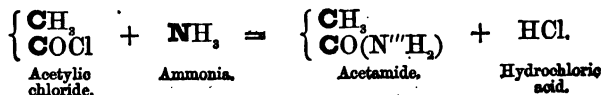
Benzamide:—



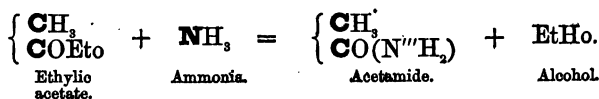
Formation.—1. By the distillation of the ammoniac salts of the monobasic acids:—



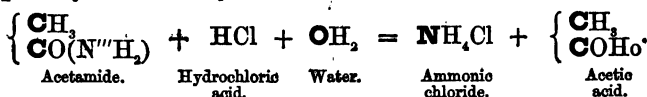
2. By the action of ammonia upon the chloracids:—



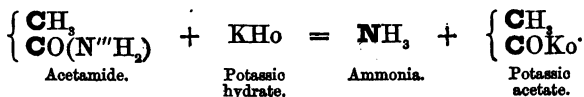
3. By the action of ammonia on the ethereal salts of the monobasic acids:—



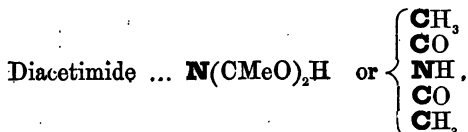
Reactions.—1. Boiled with aqueous solutions of acids, the primary monamides yield ammoniac salts and acids:—



2. Boiled with potassic hydrate, ammonia is evolved, and a potassic salt, corresponding to the amide, is formed.



II. Secondary Monamides.



These bodies possess a negative character, and are treated of under the negative section of this class as *imides of negative radicals* (p. 210).

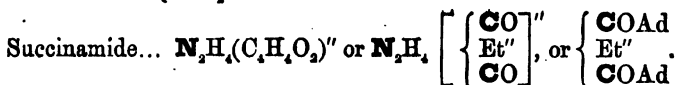
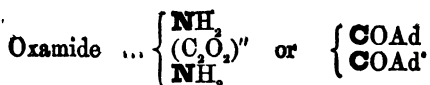
Tertiary monamides are little known. They are the *nitrides of negative radicals* (see p. 210).

B. DIAMIDES.

The diamides may be regarded as derived from two molecules of ammonia, by the substitution of a dyad negative radical for

two atoms of hydrogen; or they may be considered to be formed by the substitution of amidogen for the hydroxyl contained in the two semimolecules of oxatyl in dibasic acids:—

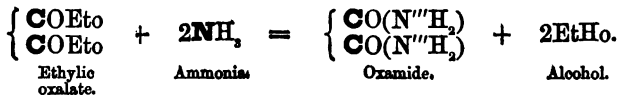
Primary Diamides.



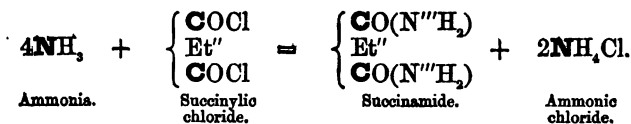
Formation.—1. By the action of heat upon the normal ammoniac salts of dibasic acids:—



2. By the action of ammonia on the ethereal salts of dibasic acids:—



3. By the action of ammonia on the chloro-dibasic acids:—

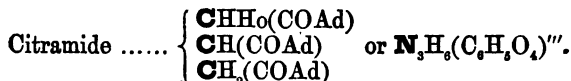


The *secondary* and *tertiary diamides* are but little known.

C. TRIAMIDES.

Primary Triamides.—The primary triamides may be regarded as derived from tribasic acids by the substitution of amidogen for the hydroxyl contained in the three semimolecules of oxatyl of these acids, or as derived from three molecules of ammonia

by the replacement of three atoms of hydrogen by the residue of a tribasic acid. A good example of a triamide is



Citramide is formed by the action of ammonia on ethylic citrate.

Secondary and tertiary triamides have not yet been formed.

2. THE ALKALAMIDES.

These compounds occupy an intermediate position between the amines and the amides. They are derived from ammonia by the substitution of part of the hydrogen by positive, and part by negative radicals; and inasmuch as two atoms at least of hydrogen must be so substituted, no primary alkalamide can exist.

Secondary and tertiary monalkalamides, dialkalamides, and trialkalamides are known.

- Ethyl acetamide $\text{NH}(\text{Et})(\text{CMeO})$.
- Ethyl diacetamide $\text{NEt}(\text{CMeO})_2$.
- Diethyl oxamide $\text{N}_2\text{H}_4\text{Et}_2(\text{C}_2\text{O}_2)''$.
- Diphenyl-carbonyl-oxalyl diamide $\text{N}_2(\text{C}_6\text{H}_5)_2(\text{CO})''(\text{C}_2\text{O}_2)''$.
- Citryl-triphenyl-triamide $\text{N}_3\text{H}_5(\text{C}_6\text{H}_5)_3(\text{C}_6\text{H}_5\text{O}_4)'''$.

The alkalamides incline towards a positive character, their degree of alkalinity being about equal to that of urea.

3. THE TRICHLORINATED AND TRIBROMINATED AMINES.

If the hydrogen in an amine be gradually substituted by chlorine or bromine, the basic character of the amine gradually diminishes, and finally a neutral compound is obtained.

This reaction has been studied in the case of aniline, which

loses basic energy by the successive replacement of two atoms of hydrogen, and finally becomes neutral by the substitution of three atoms of chlorine or bromine for three of hydrogen:—



4. THE HALOID COMPOUNDS OF OXYBASES.

These bodies are only known in the arsenic series; they are formed by the action of chlorine, bromine, or iodine upon cacodyl and its homologues, or of hydrochloric acid, hydrobromic acid, or hydriodic acid upon the oxybases.

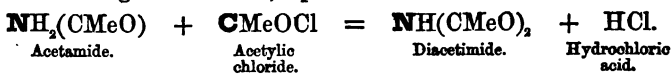
General formula..... $\text{As}(\text{C}_n\text{H}_{2n+1})_2\text{Cl}$.

NEGATIVE SECTION.

THE IMIDES AND NITRIDES.

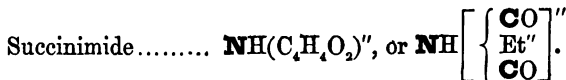
General formula... $\left\{ \begin{array}{l} \text{of imides... } \text{NH}(\text{C}_n\text{H}_{2n-1}\text{O})_2, \\ \text{of nitrides. } \text{N}(\text{C}_n\text{H}_{2n-1}\text{O})_3. \end{array} \right.$

Formation.—By the action of chloracids (the so-called chlorides of negative radicals) upon amides:—



A repetition of this reaction gives acetylic nitride, which may also be obtained by heating a mixture of acetonitrile and acetic anhydride to 200°.

An imide may also be formed by the substitution of a dyad negative radical for two atoms of hydrogen in ammonia, thus:—



These bodies have hitherto received but little attention.

CHAPTER XXX.

II. COMPOUNDS OF PENTAD NITROGEN
AND OF ITS ANALOGUES.

This class of compounds contains the following series :—

| <i>Positive.</i> | <i>Neutral.</i> | <i>Negative.</i> |
|----------------------------|--------------------------|--|
| 1. Caustic Nitrogen bases. | 1. Salts of Amines. | 1. Organic arsenic acids, oxychlorides, and chlorides. |
| 2. " Phosphorus bases. | 2. " Phosphines. | 2. Organic antimonio acids. |
| 3. " Arsenio bases. | 3. " Arsines. | |
| 4. " Antimony bases. | 4. " Stibines. | |
| 5. Oxyarsenic bases. | 5. " Oxyarsenic bases. | |
| 6. Oxyantimonic bases. | 6. " Oxyantimonic bases. | |

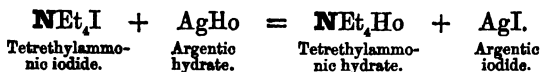
POSITIVE COMPOUNDS.

1. *Caustic Nitrogen Bases.*—

General formula..... $\mathbf{N}(\text{C}_n\text{H}_{2n+1})_4\text{Ho}$.

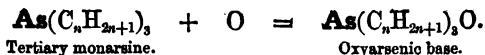
In each positive radical n must be a positive integer. The radicals need not be all of the same atomic weight.

Formation.—By the action of argentic hydrate upon the iodides of the compound ammoniums :—

2. *Caustic Phosphorus Bases.*3. *Caustic Arsenic Bases.*4. *Caustic Antimony Bases.*—

By displacing the \mathbf{N} in the above general formula and in the equation by \mathbf{P} , \mathbf{As} , and \mathbf{Sb} , the constitution and formation of these three series of compounds will be expressed.

5. *Oxyarsenic Bases.*—These bodies, which are diacid bases, are obtained by the slow oxidation of the tertiary monarsines :—

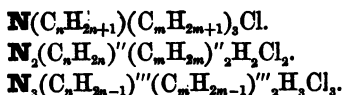


6. *Oxyantimonic Bases*.—These are formed in a manner exactly analogous to that in which the oxyarsenic bases are produced.

NEUTRAL COMPOUNDS.

1. *Salts of Amines*.

General formulæ:—



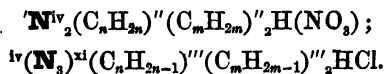
In the first formula m may = 0; in the second, C_mH_{2m} may be displaced by H_2 ; and in the third, $\text{C}_m\text{H}_{2m-1}$ may be substituted by H_3 .

Formation.—Like the analogous compounds of ammonia, the salts of the amines are formed by the direct union of acids with the amines without elimination of water, thus:—

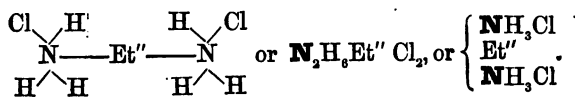


The haloid salts of the amines may also be produced by the union of the haloid ethers of the monad positive radicals with the amines (for reaction see p. 192).

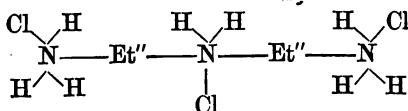
Character.—The salts of the diamines and triamines are often found to contain only one molecule of acid, instead of two or three as shown in the above general formulæ, which indicate the composition of the normal salts. The nitrogen atoms are in such cases united together by one of the bonds of each, besides being linked by the polyad radicals, thus:—



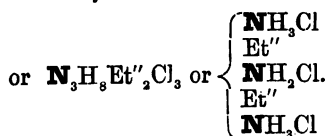
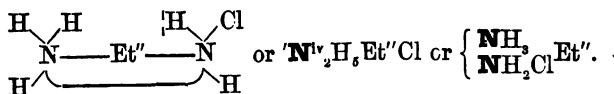
The difference between these two classes of salts will be rendered more evident by a comparison of the following graphic and symbolic formulæ:—

Normal Salts.

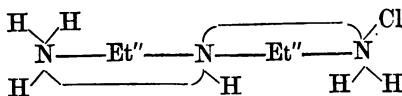
Ethylene-diammonic dichloride.



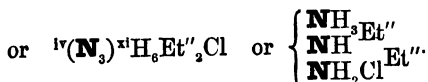
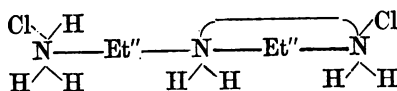
Diethylene-triammonic trichloride.

*Monacid Salts.*

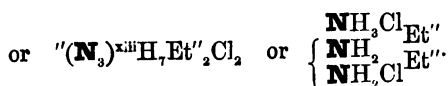
Ethylene-diammonic monochloride.



Diethylene-triammonic monochloride.

*Diacid Salt.*

Diethylene-triammonic dichloride.



214 COMPOUNDS OF NITROGEN AND ITS ANALOGUES.

2. *Salts of Phosphines.*

3. *Salts of Arsines.*

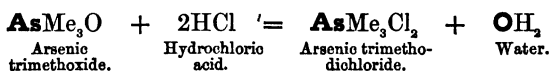
4. *Salts of Stibines.*

These three series of salts all present close analogies with the salts of the amines both in constitution and in the mode of their formation. The mode of formation of several of them is shown at pages 202 and 203.

5. *Salts of Oxyarsenic Bases.*



Formation.—By the action of acids on the oxyarsenic bases :—



6. *Salts of Oxyantimonic Bases.*

These resemble the previous salts in formation and constitution.

NEGATIVE COMPOUNDS.

1. *Organic Arsenic Acids, Oxychlorides, and Chlorides.*

The following are the principal bodies of this class :—

| | |
|---------------------------------|-------------------------------------|
| Monomethylarsenic acid..... | $\text{AsMeOH}_2\text{O}_2.$ |
| Arsenic oxydichlormethide..... | $\text{AsMeOCl}_2.$ |
| Arsenic tetrachlormethide | $\text{AsMeCl}_4.$ |
| Cacodylic acid | $\text{AsMe}_2\text{OH}_2\text{O}.$ |
| Cacodylic trichloride | $\text{AsMe}_2\text{Cl}_3.$ |

2. *Organic Antimonic Acids.*

No exploration of this series has yet been made. The members of it will doubtless be found to have close analogies with the corresponding series of arsenic compounds.

CHAPTER XXXI.

ORGANO-BORON AND SILICON COMPOUNDS.

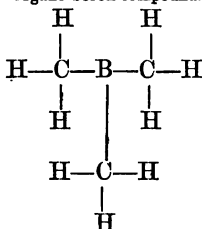
THIS family is divided into the two following classes:—

1. Organo-boron compounds.
2. Organo-silicon compounds.

1. *Organo-boron compounds.*

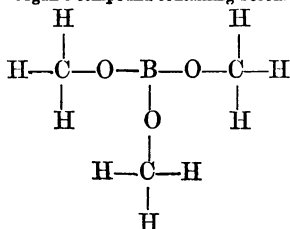
These compounds contain boron directly united with the carbon of monad positive radicals, and are thus distinguished from organic compounds containing boron, as seen in the following formulæ:—

Organo-boron compound.



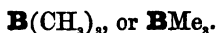
Borio methide.

Organic compound containing boron.



Methylic borate.

The organo-boron compounds are produced by the replacement of methoxyl or ethoxyl in methylic or ethylic borate by monad positive radicals. Hitherto only the radicals methyl and ethyl have been thus combined with boron.

BORIC METHIDE.

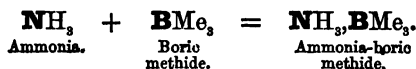
Molecular weight = 56. *Molecular volume* $\square\square$. 1 litre of boric methide gas weighs 28 criths. Condenses at 10° under a pressure of four atmospheres.

Preparation.—By adding to ethylic borate an ethereal solution of zincic methide, when boric methide is evolved as gas :—



Reactions.—1. Inflames spontaneously in air or oxygen.

2. Combines energetically with ammonia, forming ammonia-boric methide :—



3. Boric methide combines readily with potash, soda, lime, and baryta, forming compounds the composition of which is not known with certainty.

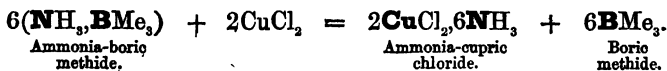
AMMONIA-BORIC METHIDE.

Molecular weight = 73. *Molecular volume* (anomalous) $\square\square$.

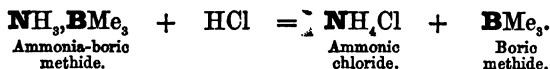
Fuses at 56°. *Boils* at 110°. 1 litre of ammonia-boric methide vapour weighs 18.25 criths.

Formed as above described.

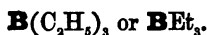
Reactions.—1. Cupric chloride absorbs ammonia from the vapour of ammonia-boric methide, reducing the volume of the vapour to one half and leaving boric methide gas :—



2. Ammonia-boric methide is readily decomposed by acids; even carbonic acid decomposes it. With hydrochloric acid the reaction is:—

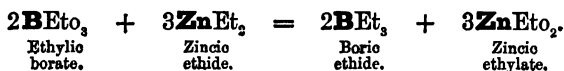


BORIC ETHIDE.



Molecular weight = 98. *Molecular volume* . 1 litre of boric ethide vapour weighs 49 criths. Boils at 95° C. Sp. gr. of liquid .6961 at 23°.

Preparation.—By the action of zincic ethide upon ethylic borate:—

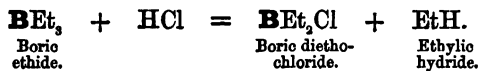


Reactions.—1. Inflames spontaneously in air, and explodes in oxygen.

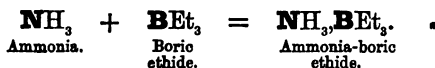
2. Allowed to oxidize gradually, boric ethide forms boric etho-diethylate:—



3. Heated with hydrochloric acid to 99°, it slowly evolves ethylic hydride, and is converted into boric dietho-chloride:—



4. Boric ethide combines very energetically with ammoniacal gas, forming ammonia-boric ethide:—

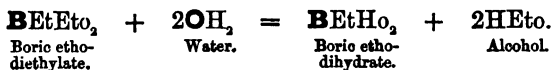


BORIC ETHO-DIETHYLATE.

Boils at 125° C.

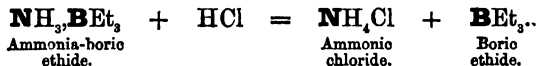
Preparation.—By the slow action of oxygen upon boric ethide as above described.

Reaction.—In contact with water it is instantly decomposed, forming *boric etho-dihydrate* :—

**AMMONIA-BORIC ETHIDE.**

Formed by the union of ammonia gas with boric ethide as above described.

Reaction.—Decomposed by acids but not by carbonic acid. With hydrochloric acid the reaction is as follows :—

**2. Organo-silicon compounds.**

The great similarity in chemical functions between carbon and silicon seems to justify the anticipation that a great number of compounds of silicon will be produced analogous in constitution to the organic compounds of carbon. Already several such compounds are known, as for instance :—

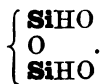
Silico-compounds.



Silicic hydride.



Silicon chloroform.



Silicoformic
anhydride.

Organic analogues.



Marsh gas.



Chloroform.



Unknown
formic anhydride.

Following the analogy of organic compounds, the substitution of one of the atoms of hydrogen in silicic hydride by the hitherto unknown radical silicon methyl (SiH_3) would yield a body constituted like the molecule of methyl or ethylic hydride,



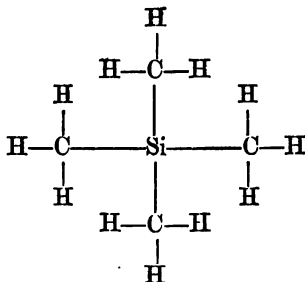
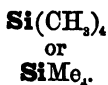
From this, silicoethylic chloride ($\text{Si}_2\text{H}_5\text{Cl}$) ought to be obtained; and then, by the substitution of hydroxyl for chlorine, the silicon-analogue of common alcohol ($\text{Si}_2\text{H}_5\text{Ho}$). None of these compounds containing silicon directly combined with silicon have hitherto been formed; indeed, unlike the tetrad elements, carbon, tin, and titanium, silicon appears to have little tendency to form such compounds. Amongst the host of silicon minerals there is not one in which the assumption of the existence of silicon combined directly with silicon is admissible. Disilicic hexachloride (Si_2Cl_6) has, however, been recently formed.

But, although these true silicon analogues of the more complex organic compounds have not hitherto been obtained, yet a large number of bodies which contain silicon atoms directly combined with carbon have been synthetically produced; and many of these substances exhibit interesting analogies with corresponding compounds containing carbon in the place of silicon. These are the bodies which are included in the class of *organo-silicon compounds*. The following Table contains the names and constitutional formulæ of the chief members of this class, together with those of their derivatives, such as ethylic silicate (SiEto_2), which do not, strictly speaking, belong to it, inasmuch as they no longer contain silicon directly combined with carbon:—

| Name. | Formula. | Boiling-point. |
|-----------------------------------|--|----------------|
| Silicic methide | SiMe_4 | 30.5 |
| Disilicic oxy-hexamethylate | $\begin{cases} \text{SiMeO}_3 \\ \text{O} \\ \text{SiMeO}_3 \end{cases}$ | 202 |

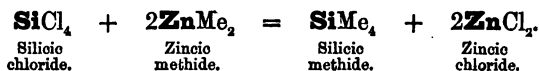
| Name. | Formula. | Boiling-point. ° |
|---|---|---------------------|
| Silicic methylate | SiMeO_4 | 121 |
| Silicic ethide..... | SiEt_4 | 152.5 |
| Silicic dimethylate ethylate..... | $\text{SiMeO}_2\text{EtO}_2$ | 145 |
| Silicic chlortriethylate | SiClEtO_3 | 156 |
| Silicic dichlorethylate | $\text{SiCl}_2\text{EtO}_2$ | — |
| Silicic ethylate | SiEtO_4 | 166.5 |
| Silicic triethylate amylate | SiEtO_3Ayo | 220 |
| Disilicic oxy-hexaethylate | $\left\{ \begin{array}{l} \text{SiEtO}_3 \\ \text{O} \\ \text{SiEtO}_3 \end{array} \right.$ | 235 |
| Disilicic oxy-hexaethide..... | $\left\{ \begin{array}{l} \text{SiEt}_3 \\ \text{O} \\ \text{SiEt}_3 \end{array} \right.$ | 227 |
| Silicic hydrotriethylate | SiHEtO_3 | 134 |
| Silicic ethotriethylate | SiEtEtO_3 | 158.5 |
| Silicic dieth-ethylate | $\text{SiEt}_2\text{EtO}_2$ | 155.5 |
| Silicic trieth-ethylate | SiEt_3EtO | 153 |
| Silicic dietho-chlorethylate | $\text{SiEt}_2\text{ClEtO}$ | 148 |
| Silicic chlortriethide..... | SiEt_3Cl | 143.5 |
| Silicic dichlorethide | SiEt_2Cl_2 | 129 |
| Silicic trichlorethide | SiEtCl_3 | — |
| Silicic diethoxide | SiEt_2O | — |
| Siliconylic chloride..... | $\left\{ \begin{array}{l} \text{SiEt}_3 \\ \text{CMeHCl} \end{array} \right.$ | 185 |
| Siliconylic alcohol | $\left\{ \begin{array}{l} \text{SiEt}_3 \\ \text{CMeHHo} \end{array} \right.$ | 190 |
| Siliconylic acetate | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CO}(\text{SiC}_2\text{H}_5\text{O}) \end{array} \right.$ | 211 |
| Silicic aceto-triethylate | $\left\{ \begin{array}{l} \text{SiEtO}_3 \\ \text{O} \\ \text{C OM} \end{array} \right.$ | — |
| Silicic acetylate | $\text{Si}(\text{COMe})_4$ | — |
| Silicopropionic acid | $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{SiOHo} \end{array} \right.$ | — |
| Silicic triethohydrate (<i>Triethyl-silicol</i>)..... | $\left\{ \begin{array}{l} \text{SiEt}_3\text{Ho} \end{array} \right.$ | 153.5 |

SILICIC METHIDE.



Molecular weight = 88.5. *Molecular volume* $\square\square$. 1 litre of silicic methide vapour weighs 44.25 criths. Boils at 30°5.

Formation.—By the action of zincic methide upon silicic chloride at a temperature of from 120° to 200°.



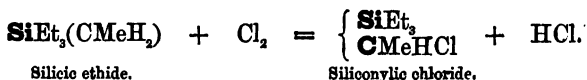
SILICIC ETHIDE.



Molecular weight = 144.5. *Molecular volume* $\square\square$. 1 litre of silicic ethide vapour weighs 72.25 criths. Boils at 152°5.

Preparation.—By the substitution of zincic ethide for zincic methide in the reaction last described, silicic ethide is produced.

Reactions.—Treated with chlorine, one atom of hydrogen is replaced by an atom of chlorine, and *siliconylic chloride* is formed:—



At the same time a portion of the silicic ethide is converted into dichlorinated silicic ethide, which, when heated with aqueous alcohol and potassic acetate, yields disilicic oxyethide,

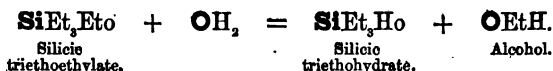


SILICIC TRIETHOXYDRATE. *Triethyl-silicol.*



Molecular weight = 132.5. *Molecular volume* $\square\square$. 1 litre of the vapour weighs 66.25 criths. Boils at 153°. *Sp. gr. of liquid* .8709 at 0°.

Preparation. 1. By digesting silicic triethoxyhydrate with water at 200°:—



2. By the action of aqueous ammonia upon silicic chlortriethide:—

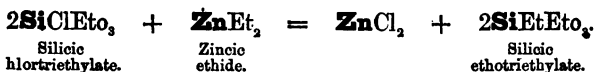


SILICOPROPIONIC ACID.

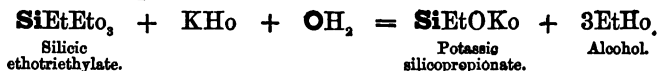


Preparation.—1. This acid, which contains the new negative radical **SiOHo** (that is to say, oxatyl in which carbon is replaced by silicon), is prepared from silicic chlortriethyle by the following series of reactions:—

1st. Silicic chlortriethyle is treated with zinc ethide and sodium, and thus converted into silicic ethotriethyle by the following reaction:—

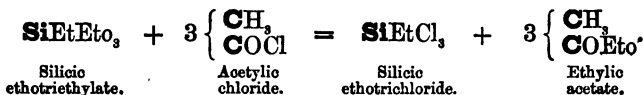


2nd. Silicic ethotriethylate, which is a colourless liquid, smelling like camphor and boiling at $158^{\circ}\cdot 5$, is now heated with concentrated solution of potassic hydrate, when the following change takes place:—

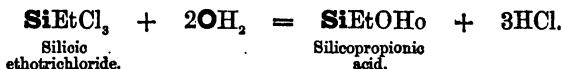


3rd. From the potassium salt, silicopropionic is obtained by the addition of hydrochloric acid.

2. By heating silicic ethotriethylate with acetylic chloride to 180° , silicic ethotrichloride is produced:—



By the subsequent action of water upon the silicic ethotrichloride, pure silicopropionic acid is obtained as a white insoluble powder resembling silica:—



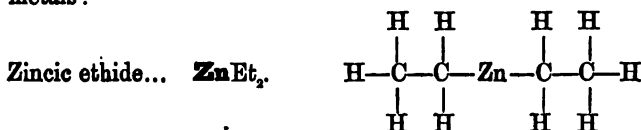
CHAPTER XXXII.

ORGANOMETALLIC BODIES.

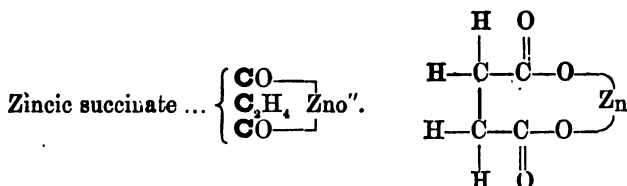
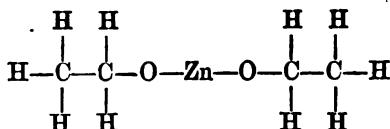
THIS term is applied to a family of compounds in which an organic radical is united directly with a metal; and it serves to distinguish them from other organic compounds containing metals, in which the metal and organic radical are indirectly united or linked to each other.

Thus zincic ethide is an organometallic body, while zincic

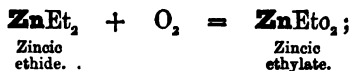
ethylate and zinc succinate are organic bodies containing metals :—



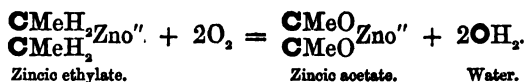
Zinc ethylate... ZnEtO_2 .



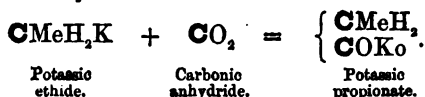
Many organic compounds containing metals are the derivatives of organometallic bodies; thus zinc ethide by oxidation yields zinc ethylate—



and by further oxidation zinc ethylate can be converted into zinc acetate—



Another instance of the derivation of organic bodies containing metals from organometallic bodies is seen in the formation of potassic propionate by the action of potassic ethide upon carbonic anhydride :—

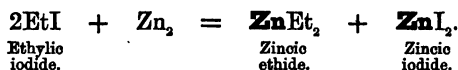


Formation of organometallic bodies.

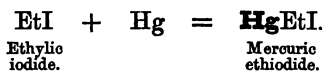
Organometallic bodies are produced in a large number of reactions, which, however, may be classed under the following four heads:—

I. By the union of monad positive radicals *in statu nascenti* with a metal, or by the coalescence of a metal with the iodide of a monad positive radical.

Thus, when zinc and ethylic iodide are heated together to 100° in closed vessels, zinc ethide is formed:—

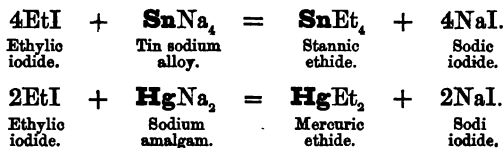


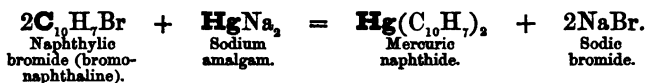
Sometimes light may be employed instead of heat to effect this change, as in the case of the organo-tin compounds. In the formation of organo-mercury compounds by this method, light is indispensable to the reaction:—



II. By the action of the respective metals alloyed with potassium or sodium upon the iodides or, in rare cases, the bromides of the monad positive radicals.

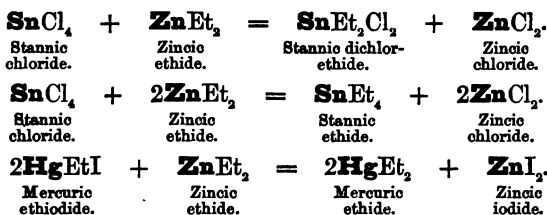
By this process there is less tendency to form compounds containing both positive radicals and negative elements. Potassium or sodium compounds are never produced in this reaction, because they cannot exist in the presence of ethylic iodide or its homologues. This process is well adapted for the formation of arsenic, antimony, tin, mercury, lead, bismuth, and tellurium compounds:—





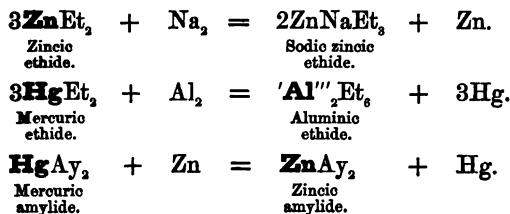
III. By the action of the zinc compounds of the monad positive radicals upon the haloid compounds, either of the metals themselves, or of their organo- derivatives.

For the production of organometallic bodies containing less positive metals than zinc, this method is generally the most convenient, and is of most universal application. Compounds containing mercury, tin, lead, antimony, and arsenic have been thus produced; but the process has failed when applied to the haloid compounds of copper, silver, platinum, and iron; for, although these bodies are violently acted upon, the organic radicals do not unite with the metal:—



IV. By the displacement of a metal in an organometallic compound by another and more positive metal.

This method has been successfully employed for the formation of the organo- compounds of potassium, sodium, lithium, aluminium, and zinc. In the first three cases the reaction takes place at ordinary temperatures, some of the original compound entering into the composition of the resulting organometallic body:—



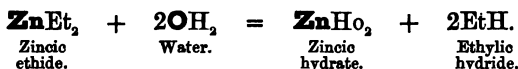
Reactions of organometallic bodies.

1. The most interesting reaction of the *organo-compounds of the monad metals* is their transformation into salts of normal fatty acids by the action of carbonic anhydride (see p. 118).

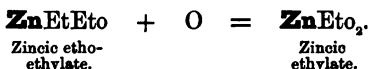
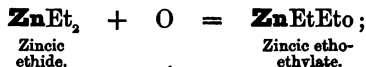
2. The *organo-compounds of potassium and sodium* decompose the iodides of the monad positive radicals in the cold, forming hydrides and dyad radicals:—



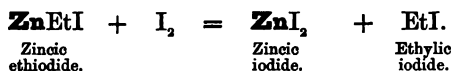
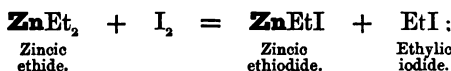
3. The *organo-compounds of zinc* are decomposed by water, with formation of the hydrides of the radicals:—



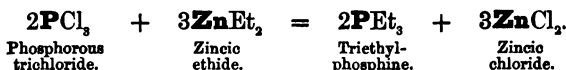
4. By the slow action of dry oxygen, they pass through two stages of oxidation:—

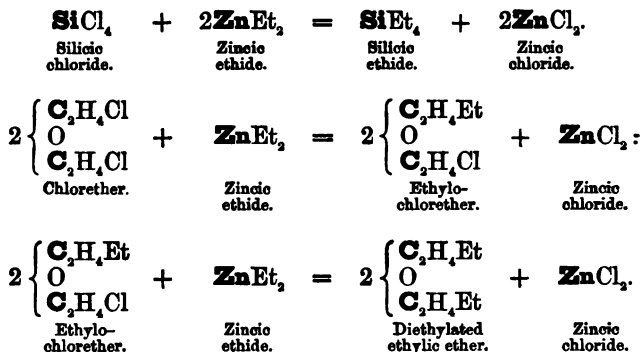


5. Monad negative elements, such as iodine, remove successively the two atoms of ethyl:—



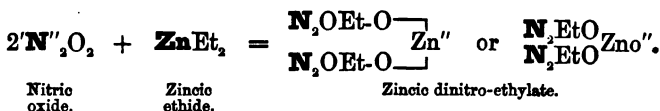
6. The *organo-zinc compounds* are extremely useful for the displacement of chlorine or its analogues by ethyl or its homologues:—



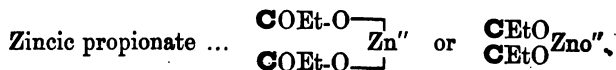


Diethylated ethylic ether is isomeric with butylic ether, and contains the radical methylo-ethylated methyl (see p. 8). By oxidation it would doubtless give methylated acetone (p. 187).

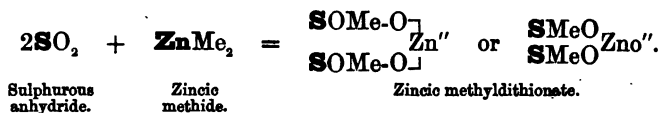
7. Oxygen may also be displaced in a similar manner. Thus:—



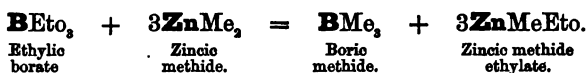
This compound is analogous to zinc propionate, the latter containing two atoms of tetrad carbon in the place of the two tetrad pairs of nitrogen atoms:—



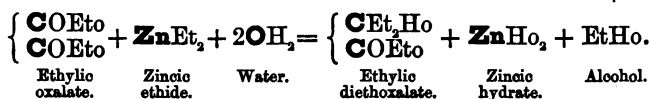
8. An analogous reaction is observed with sulphurous anhydride:—



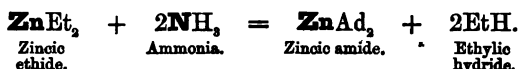
9. When ethylic borate is acted upon by zincic methide, the ethoxyl becomes replaced by methyl :—



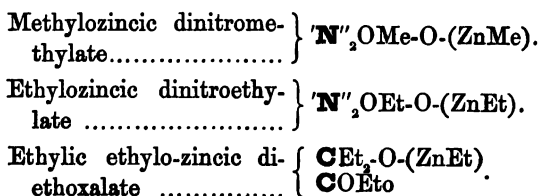
10. When ethylic oxalate is heated with zincic ethide, and water afterwards added, ethylic diethoxalate is formed :—



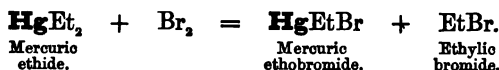
11. By the action of ammonia, or of certain amines and amides, zincic ethide exchanges its zinc for hydrogen :—



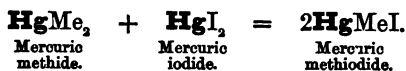
12. The organo-zinc compounds, by losing one semimolecule of their organic radical, become monad radicals, as shown by the following formulæ :—



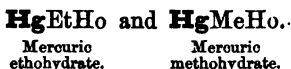
13. *Mercuric ethide*, when treated with bromine, loses one-half of its ethyl, which is displaced by the negative element :—



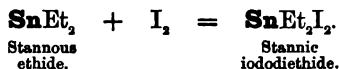
14. *Mercuric methide*, when submitted to the action of mercuric iodide, yields mercuric methiodide :—



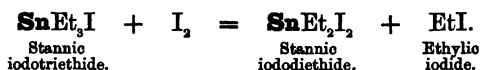
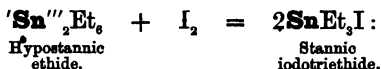
The hydrates corresponding to the mercuric ethobromide and methiodide have been produced. They are powerful caustic bases, of the formulæ



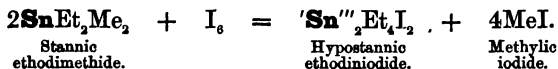
15. The *organo-stannous* compounds unite directly with negative elements, passing into stannic bodies:—



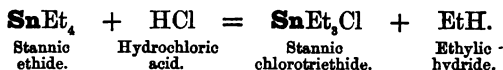
16. *Hypostannic organo- compounds* undergo a similar transformation:—



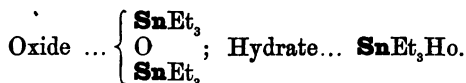
17. *Hypostannic ethodiniiodide* is formed by the action of iodine upon stannic ethodimethide:—



18. *Stannic ethide*, when treated with hydrochloric acid, yields stannic chlorotriethide and ethylic hydride:—



The oxide and hydrate corresponding to the stannic chlorotriethide are known; their formulæ are:—

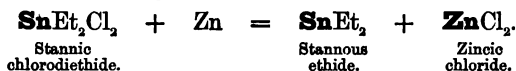


These compounds, and the salts which they form, correspond

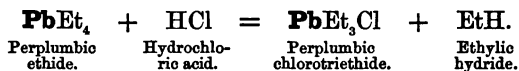
in composition, constitution, and, to a certain extent, in properties, with the compounds of methyl:—

| | Alcohol. | Haloid ether. | Ether. |
|----------------------|---------------------------|---------------------------|---|
| Methylic | $\text{CH}_3\text{Ho.}$ | $\text{CH}_3\text{Cl.}$ | $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{O} \\ \text{CH}_3 \end{array} \right.$ |
| Stanntriethylic..... | $\text{SnEt}_3\text{Ho.}$ | $\text{SnEt}_3\text{Cl.}$ | $\left\{ \begin{array}{l} \text{SnEt}_3 \\ \text{O} \\ \text{SnEt}_3 \end{array} \right.$ |

19. *Stannic chlorodiethide* is readily reduced to stannous ethide by the action of zinc:—



20. *Perplumbic ethide* resembles stannic ethide in its reactions; thus with hydrochloric acid it yields perplumbic chlorotriethide and ethylic hydride:—



21. *Perplumbic triethohydrate* (PbEt_3Ho) is a powerful base, forming salts with acids.

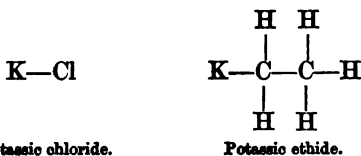
22. The *organo-tellurium compounds* form oxides and salts. The following are the formulæ of tellurium ethide and some of its compounds:—

| | |
|--------------------------------|--|
| Tellurium ethide | $\text{TeEt}_2.$ |
| Tellurous diethoxide..... | $\text{TeEt}_2\text{O.}$ |
| Tellurous diethiodide | $\text{TeEt}_2\text{I}_2.$ |
| Tellurous diethosulphate | $\text{TeEt}_2(\text{S}^{\text{VI}}\text{O})''.$ |

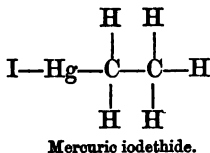
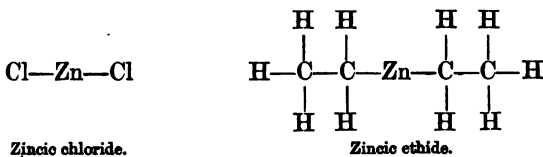
Constitution of Organometallic Bodies.

The organometallic compounds are constituted on the types of the metals they contain. It was, in fact, the study of these bodies which first led to the doctrine of the atomicity of elements. They afford striking examples of monad, dyad, triad, tetrad, pentad, and hexad types.

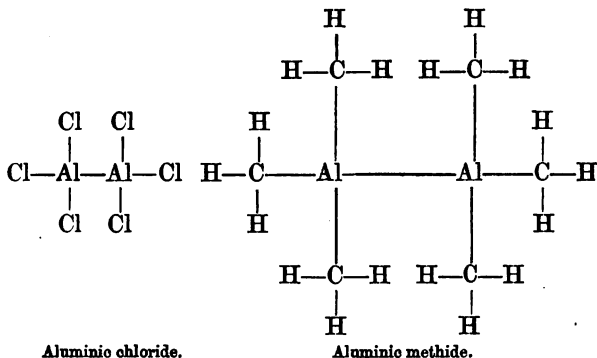
The organic derivatives of the monad metals are formed on the type of potassic chloride (KCl):—



The organo-zinc, cadmium, magnesium, and mercury compounds are formed upon the type of zincic chloride (ZnCl_2):—

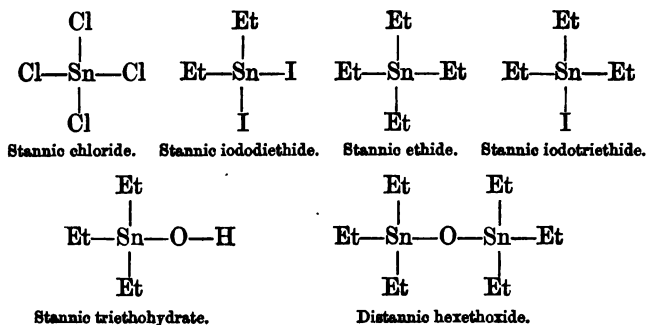


The organo-aluminic compounds are formed upon the type of aluminic chloride ($\text{Al}'''_2\text{Cl}_6$):—

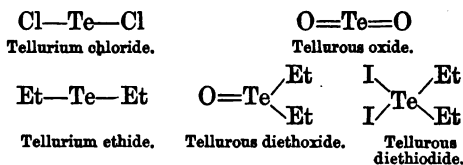


The organo-tin compounds are formed upon the three types " $\text{Sn}'''\text{Cl}_2$ ", " $\text{Sn}'''\text{Cl}_3$ ", and " SnCl_4 ",—the first resembling the zincic

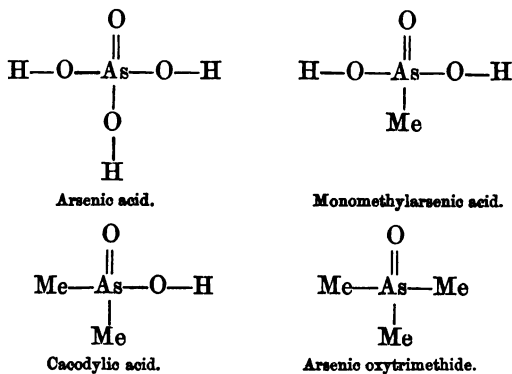
chloride type, and the second the aluminic chloride type (see p. 232) :—



The inorganic types of the organo-tellurium series are TeCl_4 and TeO_2 :—



The organo-arsenic, antimony, and bismuth compounds are derived from the types ' $\text{As}''_2\text{S}''_2$ ', AsCl_3 , AsOH_3 , SbCl_3 , SbCl_5 , BiCl_3 , and BiO_2Ho (see pp. 204, 211, and 214) :—



The effect of the substitution of positive for negative radicals in compounds is strikingly exhibited in the case of arsenic acid, AsO_3H_3 , as illustrated in the above graphic representations. By the substitution of one semimolecule of methyl for hydroxyl, a well-defined acid (less negative, however, than arsenic acid) is produced, monomethylarsenic acid, AsOMeH_2 . By the replacement of a second semimolecule of hydroxyl by methyl, a very feeble acid, cacodylic acid, AsOMe_2H , is obtained. By the replacement of the third semimolecule of hydroxyl by methyl, the acid properties are completely destroyed, a feeble base, the arsenic oxytrimethide, being formed, AsOMe_3 . Finally, by the substitution of methyl and hydroxyl for the remaining atom of oxygen there is produced a powerful base, tetramethylarsenic hydrate, AsMe_4H .

The following is a list of the principal organometallic bodies at present known :—

I. Organo- compounds containing monad metals :—

| | |
|------------------------------|--------------------------------|
| Potassio-zincic methide..... | $\text{KMe}, \text{ZnMe}_2$. |
| Potassio-zincic ethide | $\text{KEt}, \text{ZnEt}_2$. |
| Sodio-zincic ethide..... | $\text{NaEt}, \text{ZnEt}_2$. |
| Lithio-zincic ethide | $\text{LiEt}, \text{ZnEt}_2$. |
| Lithio-mercuric ethide | $\text{LiEt}, \text{HgEt}_2$. |

II. Organo- compounds containing dyad metals :—

| | |
|---------------------------|---|
| Magnesium ethide..... | MgEt_2 . |
| Zincic methide | ZnMe_2 . |
| Zincic ethide | ZnEt_2 . |
| Zincic amylide | ZnAy_2 . |
| Mercuric methide | HgMe_2 . |
| Mercuric ethide | HgEt_2 . |
| Mercuric methiodide | HgMeI . |
| Mercuric ethonitrate..... | $\text{HgEt}(\text{N}^{\circ}\text{O}_3)$. |
| Stannous ethide | " Sn " Et_2 . |
| Tellurium methide | TeMe_2 . |

III. Organo- compounds containing triad metals :—

These compounds belong to the 11th family of organic bodies, and have been treated of at p. 202.

IV. Organo- compounds of tetrad metals :—

| | |
|-------------------------------------|---|
| Stannic methide | SnMe₄. |
| Stannic iodotrimethide | SnMe₃I. |
| Stannic iododimethide | SnMe₂I₂. |
| Hypostannic ethide | 'Sn'''₂Et₆. |
| Stannic ethylodimethide | SnEt₂Me₂. |
| Stannic phenyl-triethide | SnPhEt₃. |
| Stannic ethophenyl-dichloride | SnPhEtCl₂. |
| Hypostannic ethodiiodide | 'Sn'''₂Et₄I₂. |
| Perplumbic ethide | PbEt₄. |
| Perplumbic chlorotriethide | PbEt₃Cl. |

V. Organo- compounds of pentad metals :—

These bodies belong to the 11th family of organic compounds, and have been already treated of at pp. 211 and 214.

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